INORGANIC CHEMISTRY

WITH THE ELEMENTS OF PHYSICAL AND THEORETICAL CHEMISTRY

BY

J. I. D. HINDS, Ph.D.

Professor of Chemistry in the University of Nashville

SECOND EDITION, THOROUGHLY REVISED

FIRST THOUSAND

NEW YORK

JOHN WILEY & SONS

LONDON: CHAPMAN & HALL, LIMITED

1908.

PREFACE.

THIS volume is intended to supply a rather complete text-book on inorganic chemistry for colleges and universities, and a handy reference book for all students and teachers of chemistry. I have had in mind first an orderly and systematic treatment of the sub- ject without reference to any teaching method. The teacher may go from chapter to chapter as his own method may require.

In writing the book I have gathered information from any source within my reach, and here fully acknowledge my indebted- ness to the many authors whose works I have consulted, to the dictionaries of chemistry, and to the various chemical journals. Special thanks are due to Messrs. Longmans, Green and Company for the use of Figs. 5, 37, 50, and 61, taken from Newth's Chem- istry, and to the *Scientific American* for Fig. 69.

In Part I is found a general introduction to chemistry and a logical division of the subject into its principal branches.

In Part II is given such an outline of physical chemistry as is necessary to the full understanding and appreciation of the de- scriptive portion of the work.

In Part III theoretical chemistry is treated with more than the usual fullness. The student cannot too soon become acquainted with this branch of the subject nor study it too much. It contains the very heart of chemistry, and a knowledge of it is absolutely necessary to the intelligent study of the elements and their com- pounds.

In Part IV the purpose has been to treat with the fullness which it deserves every known chemical element and all the com- pounds which are of commercial or of theoretical interest. In classification and treatment the periodic system has been closely

iii

followed, since after due consideration this plan seemed most con-
venient as well as most scientific.

Atomic weights are given in the tables with reference to both
hydrogen and oxygen, but in the text the oxygen values are used
because they are most familiar and most nearly approximate whole
numbers.

A laboratory handbook has been prepared to accompany this
volume.   The student should do the work indicated therein as in-
dustriously as he studies this text.

<div align="right">J. I. D. HINDS.</div>

UNIVERSITY OF NASHVILLE,
  NASHVILLE, TENNESSEE,
      September, 1902.

PREFACE TO THE SECOND EDITION.

THE thorough revision which has been made for this edition
has necessitated the rearrangement of some of the parts and chap-
ters.   Fuller treatment has been given to Theoretical and Physical
Chemistry and several of the chapters have been largely rewritten;
as, for example, those on Chemical Actions, Solutions and Thermo-
chemistry.   New chapters have been added on Electrochemistry
and Photochemistry, including Radioactivity, thus making the
treatment of Physical Chemistry, though brief, practically com-
plete.   In the Part on Descriptive Chemistry errors have been
removed so far as they have been discovered, and such minor
changes and additions have been made as to secure harmony with
the present state of chemical knowledge.   Ions have received due
consideration and a chapter has been added on Radium, Polonium,
and Actinium.

In addition to the very full index with which the volume closes,
a Biographical Index has been prepared which should be helpful to
both students and teachers of chemistry.

<div align="right">J. I. D. HINDS.</div>

January, 1905.

SUGGESTIONS TO TEACHERS.

A TEACHER's method cannot well be put into a text-book, but the text-book can accommodate itself to the teacher. I suggest three courses, either of which, I think, may be successfully followed with this volume.

1. Follow the laboratory book for the first two or three months, studying in this book the subjects treated there.

2. Study Part I, then begin Part IV, but take one lesson each week from Parts II and III.

3. Study the chapters and subjects in the following order :

Chapters I, III, IV, V, hydrogen, oxygen, water; Chapters VII, IX, X, chlorin, hydrochloric acid, sulfur, hydrogen sulfid, nitrogen, ammonia, nitric acid, carbon, carbon dioxid, carbon monoxid, sodium, sodium chlorid, sodium hydroxid, potassium, calcium, aluminum; Chapters VI, XI; then through the book regularly, beginning at Part II.

▼

CONTENTS.

vii

INORGANIC CHEMISTRY.

PART I.

INTRODUCTION.

CHAPTER I.

GENERAL STATEMENTS AND DEFINITIONS.

Science.—The word science means knowledge. The term is widely applied to all classified knowledge. Its use is, however, generally limited to the study of material things.

Material science is knowledge obtained directly or by inference from nature. It is divided into two branches, *physical science* and *natural science*.

Physical science studies matter itself and includes the two subjects, *physics* and *chemistry*.

Natural science studies material forms and structures and includes the biological sciences of zoology and botany.

Astronomy, geology, mineralogy, and geography are mixed sciences, being neither purely physical nor purely natural, but partaking of the nature of both.

Statics and Dynamics.—In all science work an object may be studied at rest or in action. In the one case we study structure, properties, characteristics; in the other, function, use. There are thus two divisions of any science which may be called *statics* and *dynamics*. In biology they constitute the two great divisions called morphology or anatomy and physiology.

Matter Defined.—Matter is that which composes the objective universe and which we perceive through the senses. It does not, however, follow that all matter may be perceived. We have reason to believe that there are forms of matter not perceptible as such; as, for example, the interstellar ether.

Matter Indestructible.—So far as we know, matter cannot be created nor destroyed. When it apparently disappears. it has simply changed its form. In the combustion of wood or coal, for example, if the products of the combustion, some of which are invisible gases, together with the ash, be collected and weighed, it will be found that nothing has been lost. Chemistry has mainly to do with transformations of matter and as an exact science is based upon the indestructibility of matter.

States of Matter.—Matter exists in three states, *solid, liquid,* and *gas.* In solids the molecules are held rigidly together; in liquids they yield easily to an external force and move slowly among themselves; in gases they are widely separated and move with the greatest freedom. There is no sharp line between the three states. We have soft solids and viscous liquids, and some gases under pressure may be brought very near to the liquid condition.

Theoretically any substance may be made to exist in each of the three states, and in most cases this can be done practically. A familiar example is ice, water, and steam. Iron may be melted and gasified, and air may be liquefied and solidified.

Molecules and Atoms.—According to theories which will be explained later, matter is composed of molecules and atoms. If a portion or mass of matter be divided continually a particle will finally be reached which cannot be divided without destroying the identity of the substance. This particle is called a *molecule.* The molecule itself is composed of smaller particles which may be like or unlike, and these are called *atoms.* The relative weights of these ultimate particles have been determined for the various kinds of matter, and are called respectively *molecular weight* and *atomic weight.*

Size of Molecules.—The molecule is exceedingly small. Its size has been computed by various physical methods. For example, a study of the colors produced by the interference of light in soap-bubbles has shown that the average diameter of the molecule is less than half the wave-length of light. If 5,000,000 of them were

laid side by side they would make a line about 1 cm. long.   A cubic centimeter of gas at 0° temperature and under a pressure of 760 mm. of mercury contains about 2×10^{19}, or twenty million million million molecules.   In the liquid and solid states the volume is 100 to 2000 times smaller.   A particle of dust barely visible to the naked eye contains more molecules than there are people on the earth.   Lord Kelvin calculated that if a drop of water were magnified to the size of the earth the molecules, correspondingly enlarged, would be smaller than cricket balls, but larger than small shot.

Illustrations.—To show the extreme smallness of the molecule dissolve in water, with the help of a little alcohol if necessary, a very small bit of some coloring matter, such as carmine or methyl violet, and dilute to half a liter.   The color will be found diffused throughout the whole of the liquid and every drop however small will be found to contain some portion of· it. If the amount taken was one centigram, a drop of the water will contain less than one millionth of a gram.

Molecular Interspaces.—When we speak of the size of the molecule, we mean the distance between the centers of adjacent molecules.   It is quite certain that the molecules are not only not in contact, but that there are comparatively large spaces between them.   Among the proofs of this we may mention the following:

1. All solids and liquids are compressible and gases are easily reduced to one half or one third of their volume by pressure.

2. Liquids dissolve solids and solids absorb liquids without material change of volume.

3. Increase of temperature causes most substances to expand, while lowering the temperature causes them to contract.

Illustrations.—Close the valves of the air-pump and force the piston down: the air is compressed.   Add slowly fine salt to a beaker full of water: see how much may be added before the water runs over.   Place a cubic centimeter of water in a watch-glass and add a lump of cut loaf sugar: the water is absorbed by the sugar.   Mix ten cc. of water with ten cc. of alcohol and measure the mixture.   Fill with water to the neck a half-liter flask and mark the surface of the water.   Heat to boiling and again note the surface.

Molecular Motion.—Molecules are not fixed, but have a more or less free motion within their interspaces.   Upon this motion depends a variety of physical phenomena, such as heat, light, and electricity; and also the physical state of bodies, viz., solid, liquid, or gas.

Number of Atoms in the Molecule.—The number of atoms a molecule may contain is exceedingly various. Sometimes it is only one, as in mercury, sometimes two, as in many elemental molecules. In compounds the number may run even to hundreds. In water there are three atoms in the molecule, in alcohol nine, in sugar forty-five, in albumen more than two hundred.

Size of the Atom.—The atom must be very much smaller than the molecule because molecules of the same size contain various numbers of atoms. It is indeed probable that the spaces between the atoms are relatively quite large and that the atoms are continually in active motion within the molecule.

Weight of Molecules and Atoms.—Knowing the size of the molecule, we are able to compute its weight; and knowing its weight and the number of atoms it contains, we can find the weight of the atom. Dealing with things so small, the determination can have but little accuracy. A cubic centimeter of hydrogen weighs 0.00009 gram. Divide this by the number of molecules it contains, 2×10^{19}, and we have 45×10^{-25} grams for the weight of one molecule of hydrogen, and one half of this is the weight of one atom.

Conditions.—A substance may exist under various conditions. Those conditions which are most important are temperature, pressure, solution, electric state, and association with other substances. The condition is not essential. It may be changed, the substance remaining the same.

Properties.—By the term properties we mean certain characteristics or peculiarities which belong to substances. We may distinguish general properties of matter, such as extension, density, color, weight; and special properties of particlar substances, such as the yellow color of sulfur, the bitter taste of quinine, the cubical crystalline form of common salt.

Special properties are essential. They are in some way inseparably connected with the substance. Sugar could not be sugar without being sweet, and sulfuric acid could not exist without being sour.

Properties are not only qualitative, but they are quantitative and subject to measurement. This measurement affords the best means of distinguishing between substances.

Physical properties are those which relate to masses and molecules. They are the properties with which we are most familiar,

such as extension, weight, color, hardness, and divisibility. *Chemical properties* depend upon the nature of the substance or the composition of the molecule. They are such as tend to give rise to chemical action and chemical change. Combustibility, acidity, alkalinity, and power of bleaching are chemical properties.

Identification of Substances.—Substances are identified by their properties. By *substance* we mean a' *kind* or *species* of matter which, wherever it exists, will under similar conditions exhibit the same set of properties. Since it is impossible to investigate all properties, we seek a few and, finding agreement in these, we infer that there is agreement in all. For example, if I find two bodies to agree in being yellow, brittle, crystalline, insoluble in water, fusible at a moderate temperature, and combustible, burning with a blue flame and yielding a gas of stifling odor, I conclude that they are of the same substance, sulfur. This method of reasoning is *inductive.* Its modern development and its association with systematic experimentation is due to Francis Bacon.

Induction.—Inductive reasoning is based upon the *law of uniformity in nature,* and this law is itself an induction from universal human experience. As applied to the problem of identifying substances, the law may be stated thus:

When two substances agree exactly in a number of their properties, they will also agree in all their properties.

This conclusion is not *necessary,* because exceptions might exist. The strength of the conclusion depends upon the number and importance of the properties investigated.

Laws.—A law is simply a statement of agreement between facts of a certain class, and is an induction from observation and experience. The law of gravitation, for example, is "All bodies attract one another with a force which varies directly as the mass and inversely as the square of the distance between them." Every observation of an accordant fact helps to establish the law more firmly.

Theories.—A theory is an attempt to explain a law or a series of facts. The truth of a theory increases in probability as the number of facts which it explains increases and the number which it fails to explain diminishes. For illustrations the student is referred to the laws and theories discussed later.

Physics and Chemistry.—Physics and chemistry are very closely

related and most actions which are called chemical have also physical features. Indeed, the relationship is such that there has developed a new intermediate science called *Physical Chemistry.* There are, however, so many facts and phenomena which are characteristically either physical or chemical that the separate treatment of the two subjects is amply justified. The statements or definitions given below will be useful to the student, though their full meaning will not be apprehended until later.

Physics treats of the properties, actions, and changes of position, state, or condition of matter as masses and molecules.

Chemistry treats of specific substances, elementary and compound, and studies the properties, actions, and conditions which are essential to the substance, or which depend upon the atomic composition of the molecule.

A *physical change* is one which changes the state or condition of the substance without changing its identity.

A *chemical change* is one which affects the composition of the molecule and therefore destroys the identity of the substance. It is always marked by the disappearance of one or more substances and the appearance of others.

A *physical action* is one which produces physical change, and a *chemical action* is one which produces chemical change.

Illustrations.—Melt a piece of ice and convert it into steam: physical change and the three states of matter. Put into a test-tube a gram of potassium chlorate and heat strongly: it melts, physical change; it decomposes, giving off a gas, chemical change; the gas causes an ignited splinter to burst into flame showing it to be oxygen. Drop a splinter or match-stick in the tube while hot: a violent combustion of the wood in oxygen ensues, chemical change, and chemical action.

CHAPTER II.

DIVISIONS OF CHEMISTRY.

The subject of chemistry is divided for the sake of convenience and scientific treatment into several parts. The first natural division is into Pure Chemistry and Applied Chemistry.

Pure Chemistry treats the science as a branch of pure knowledge and studies facts, phenomena, and methods without special reference to practical utility. It has four principal divisions: Theoretical Chemistry, Descriptive Chemistry, Practical Chemistry, and Analytical Chemistry.

Theoretical Chemistry treats of the general principles of the science and seeks to find a rational explanation of all chemical facts and phenomena. This subject has two principal divisions, Chemical Statics and Chemical Dynamics.

Chemical Statics includes such subjects as theory of atoms and molecules, atomic weight, valence, electric quality, atomic and molecular volume, molecular structure, etc.

Chemical Dynamics treats of such subjects as reactions, equations, thermics, photochemistry, and chemical properties in general.

Descriptive Chemistry gives a description of all the elements and their compounds with their properties, physical, chemical, and physiological. The description should include occurrence, discovery, history, preparation, properties, uses, tests, reactions. The division of descriptive chemistry into Inorganic and Organic is an arbitrary one made for convenience of treatment.

Practical Chemistry treats of chemical manipulations, operations, and methods. Applied chemistry and analytical chemistry are largely practical, and descriptive chemistry involves many practical operations. Theoretical chemistry is based upon the other three branches.

7

Analytical Chemistry treats of the methods of ascertaining the chemical composition of substances and mixtures both as to kind and quantity. It has two divisions, Qualitative Analysis and Quantitative Analysis.

Qualitative Analysis is that branch of the science which has for its object the determination of the kinds of elements and compounds which are contained in substances of unknown composition. It is based mainly upon chemical dynamics and involves a complete knowledge of descriptive chemistry. Any chemical action, phenomenon, or operation may furnish evidence, but those most used are solution, solubility, color, and precipitation. Heat and light are helpful agents. The principal agent in Blowpipe Analysis and Assaying is heat, and in Spectroscopic Analysis it is light.

Quantitative Analysis has for its object the determination of the amount of each element and compound contained in any given substance. According to the method employed it has four divisions: Gravimetric, Volumetric, Colorimetric, and Photometric.

Gravimetric Analysis is the process in which the quantities are determined by actual weighing. The substance to be analyzed is weighed. It is then converted by chemical action into substances of known composition. These are separated and weighed and then by computation the quantities in the original substance are ascertained.

Volumetric Analysis is that process in which the reagents are used in solutions of known strength. The quantity of the solution required to completely precipitate or change the substance to be determined indicates the quantity of the substance present.

Colorimetric Analysis determines quantities by the depth of color imparted by the reagent to the solution. This method is of limited application.

Photometric Analysis ascertains quantities by the depth of a column of water containing a suspended precipitate through which a flame is just invisible.

Applied Chemistry is the basis of a great number of practical arts. Among them are metallurgy, photography, agriculture, the manufacture of chemicals, drugs, foods, and drinks. Indeed, almost every art and industry is more or less dependent upon the science of chemistry. Chemistry embraces a larger field of study

and touches more points of human interest than any other science, and we may possibly say than all other sciences together.

Physical Chemistry.—To this classification may be added the related branch called Physical Chemistry. This includes so much of the science of physics as is intimately connected with chemical operations, actions, and phenomena.

SUMMARY OF THE DIVISIONS OF CHEMISTRY.

A. Pure Chemistry.
 1. Theoretical Chemistry.
  a. Chemical Statics.
  b. Chemical Dynamics.
 2. Descriptive Chemistry.
  a. Inorganic Chemistry.
  b. Organic Chemistry.
 3. Practical Chemistry. .
 4. Analytical Chemistry.
  a. Qualitative Analysis.
  b. Quantitative Analysis.
   1. Gravimetric.
   2. Volumetric.
   3. Colorimetric.
   4. Photometric.
B. Applied Chemistry.
C. Physical Chemistry.

CHAPTER III.

PROPERTIES RELATING TO MASSES.—MOLAR PHYSICS

Extension.—Since matter occupies space it has extension and may be measured. The extent of a body in one direction is called *length;* in two dimensions, *surface;* and in three dimensions, *volume.* The unit of length is the meter, the unit of surface is the square meter, and the unit of volume is the cubic meter. For convenience a smaller unit of volume, the liter or cubic decimeter, is in general use.

There is no natural unit of extension. Various arbitrary units have been chosen. Of these the most important are the *yard,* which is the basis of the English system, and the *meter,* which is the basis of the French system. The metric system has the advantage of being decimal and is generally used in scientific operations.

The meter is the one ten-millionth part of a quadrant of the earth's circumference, and was determined under the direction of the French government by the actual measurement of an arc of a meridian passing through France. It is equal to 39.3704 inches, or a little more than a yard. The standard meter is a platinum rod in the French archives at Paris. Official copies of it are kept in various parts of the world.

The meter is divided into ten, one hundred, and one thousand parts called respectively *decimeter, centimeter,* and *millimeter.* The multiples of the meter are the *dekameter, hectometer,* and *kilometer.* The kilometer is 0.62 of a mile.

The units most used in chemical operations are the centimeter

and the millimeter and their squares, the liter, and the cubic centimeter.

Illustration.—The decimeter is about four inches; a centimeter is about two fifths of an inch; an inch is about two and a half centimeters ; a liter is about a quart; a pint is about half a liter or 500 centimeters.

MILLIMETERS   CENTIMETERS

INCHES

Fɪɢ. 1.—Sᴄᴀʟᴇꜱ ᴏꜰ Cᴇɴᴛɪᴍᴇᴛᴇʀꜱ ᴀɴᴅ Iɴᴄʜᴇꜱ.
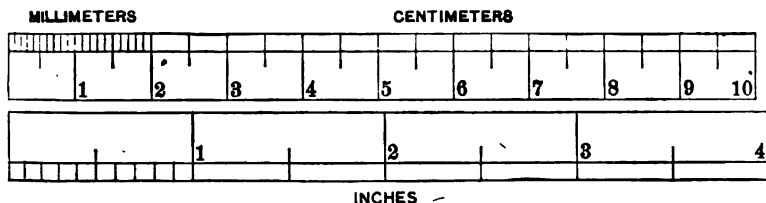
Measurements.—Lengths are ascertained by the use of ruler, tape-line, or chain. When the measure cannot be applied to the object, the length is taken with calipers or dividers and these applied to the measure. Areas are found in the same way, the dimensions being taken and the areas computed.

The volumes of regular solids are obtained by measure and cal- culation. If the solid is irregular, it is immersed in water and the amount of water displaced measured. If the specific gravity of the body is known, its volume may be found by weighing it and dividing its weight in grams by its specific gravity. The quotient will be the volume in cubic centimeters.

Liquids are measured in graduated vessels. Those most used are flasks, cylinders, graduates, pipettes, and burettes. The readings are taken at the lower surface of the meniscus. All liquid measures·are somewhat inaccurate because the volume of a liquid changes with its temperature. The capacity of the measur- ing vessel is also changeable. Where great precision is required liquids should be weighed instead of measured.

Remark.—Let the student use a meter measure and graduated vessels until he is familiar with the common units and can estimate at sight lengths, areas, and volumes with considerable accuracy.

Weight.—The weight of a body is the measure of the intensity of the earth's attraction for it. This varies on different portions of the earth's surface, being slightly greater at the poles than at the equator, and less on mountains than at the sea-level. In most operations this difference may be neglected.

The unit. of weight is the gram. This is the weight of one cubic centimeter of water at the temperature of 4° C. This is the temperature at which water has the greatest density. A gram is equal to 15.43 grains. Its decimal multiples are called dekagram, hektogram, and kilogram. It is divided into decigram, centigram, and milligram. A kilogram is equal to 2.2046 pounds.

Weight is determined by means of scales and balances.

Illustrations.—A pound is about 500 grams; a kilogram is about two pounds; an ounce is 28 grams; a gram is 15 grains; a nickel five-cent piece weighs five grams; a silver dollar weighs 26.7 grams; a $20 gold piece weighs 33.4 grams.

Scales.—Scales are of two kinds. In the first kind the weight is indicated by the amount of extension produced in a spiral spring. Within certain limits such scales have a considerable degree of accuracy. They are very liable to permanent changes and the zero-point must be frequently adjusted.

The other kind of scales is essentially a lever of unequal arms with movable weights. The object to be weighed is supported on the shorter arm, while the weights move on the longer arm. Such scales do not possess a high degree of accuracy, but they are commonly used because of their convenience and the rapidity with which the weighing can be done. Their chief advantage lies in the fact that the weight of heavy bodies may be ascertained by the use of small weights.

The Balance.—The balance is the most accurate instrument for determining weight. It is a lever of equal arms, supported on a pivot, and the object to be weighed is balanced on one arm against standard weights on the other. Its sensitiveness is only limited by friction and certain other disturbing conditions, such as changes of temperature, currents of air, etc. For rough weighing a common balance with weights from one gram to 1000 grams is used. For chemical purposes a much more delicate instrument is needed, one which weighs to the ten-thousandth or even the hundred-thousandth of a gram.

FIG. 2.—LABORATORY BALANCE.

Mass.—Mass is the quantity of matter which a body contains.

The weight of a body varies with its location and the surrounding conditions; its mass is invariable. The variation of the weight on the earth's surface is so small that weight may be taken as the measure of mass. Weights may therefore be regarded as standard masses. All mass determinations are relative. When we say that a body weighs 5 grams we simply mean that the mass of the body is five times that of the gram weight.

Density and Extensity.—Density means the quantity of matter contained in a unit of volume. It is therefore equal to the mass divided by the volume. Extensity is the volume of a unit quantity of matter. It is equal to the volume divided by the mass and is the reciprocal of density.

Illustrations.—A cubic centimeter of water at 4° C. weighs one gram. The density of water is therefore one gram per cubic centimeter. A cubic centimeter of iron weighs 7.7 grams; its density is 7.7 grams per cc. So also the volume of one gram of iron is equal to $1 \div 7.7 = 0.13$ cc.

Relative Density.—In stating densities it is convenient to have some standard substance to which all other bodies may be referred. The density of a substance in terms of the standard is called its *relative density*. Relative density is the quotient obtained by dividing the mass of the body by the mass of the same volume of the standard. It is simply the number of times heavier or lighter the substance is than the standard if we take weight to be the measure of mass. The standard of density is water for solids and liquids, and air or hydrogen for gases. When density is referred to water or air, it is called *specific gravity;* when it is referred to hydrogen, it is called *vapor density,* or better *gas density.* The volume in cubic centimeters occupied by a gram of a substance is called its *specific volume.*

Specific-gravity Determinations.—The specific gravity of a solid or a liquid is its relative density compared with pure water at 4° C. It is obtained by dividing the weight of a certain volume of the substance by the weight of the same volume of water. There are various methods, of which those given below are the principal ones. In every case two things are to be found, the volume and the weight. If we take the volume in cubic centimeters, then, since a cubic centimeter of water weighs one gram,

$$\frac{\text{Weight in grams}}{\text{Volume in cubic centimeters}} = \text{Specific Gravity.}$$

The methods are direct or indirect.

Direct Methods.—FOR SOLIDS.—If the solid is regular, its volume is obtained by direct measurement; if it is irregular, it is immersed in water and the displaced water measured or weighed. If the body is soluble in water, a liquid is used in which it is insoluble and whose specific gravity is known.

FOR LIQUIDS.—The liquid is weighed in a graduated vessel containing a fixed quantity; or it is weighed in a vessel and then the capacity of the vessel ascertained by measuring or weighing the distilled water required to fill it.

Illustrations.—1. *The volume fixed.*—The little vessel called the *pyknometer* or *specific-gravity bottle* is a small bottle with a capillary perforation through the stopper. It is made of such size as to contain a given quantity of distilled water, say 25, 50, or 100 grams. Counterpoise the dry bottle on the balance with weights, shot, or sand. Fill with the liquid so that the surface stands in the capillary at the mark on the stopper, wipe dry and weigh. This weight divided by the capacity of the bottle is the specific gravity.

2. *The volume to be found.*—Counterpoise a small flask, fill to a mark with the liquid and weigh. Empty the flask, fill it with water and weigh again. Divide the first weight by the second for the specific gravity. The volume may also be found by pouring the liquid after it is weighed into a graduated vessel, but measurement is not so accurate as weight.

Indirect Methods.—There are three indirect methods of determining specific gravity, two of them applicable to solids and the other to liquids.

FOR SOLIDS.—1. The first method consists in weighing the body in air and then in water. The loss in weight is the weight of the water displaced, or the weight of a volume of water equal to the volume of the body. The quotient obtained by dividing the weight of the body by this loss in weight is the sp. gr.

Illustrations.—Suspend the body by a fine thread to one arm of a balance and weigh. Bring a vessel of water under the body so that it is immersed and weigh again. Subtract the second weight from the first and divide the first weight by the remainder: the quotient is the sp. gr.

2. In the second method the pyknometer is used, and it might be called direct rather than indirect. It is especially adapted to bodies in a finely divided state, in powder or crystals. Counterpoise the bottle, add a weighed quantity of the substance, fill to the mark with water and weigh. This weight will be equal to the

weight of the substance plus the capacity of the bottle minus the weight of a volume of water equal to that of the substance.

FOR LIQUIDS.—Hydrometers. The instrument used in the indirect determination of the specific gravity of liquids is called the *hydrometer* or *densimeter.* It consists of a cylindrical body loaded below with mercury or shot and terminating above in a slender stem. The stem is empirically graduated to show the specific gravity. The hydrometer floats with the stem upright, and the reading is taken just below the surface of the liquid.

Some hydrometers are so graduated as to give the specific gravity directly, while others require calculation or the use of a table. The former are greatly to be preferred and are now generally used. Of the latter the most common are those of Twaddle and of Beaumé.

The reading of the Twaddle hydrometer is multiplied by 5, the product regarded as thousandths and the unit prefixed. For example, if the reading is 22 the sp. gr. is 1.120. With the Beaumé hydrometer the sp. gr. is taken from a specially prepared table.

Hydrometers are also made to be used with particular liquids or solutions. Such instruments usually indicate per cent. They are made for milk, alcohol, acids, alkalis, coal-oil, etc.

Temperature Corrections.—In all nice specific-gravity determinations regard must be had to the temperature, because the specific gravity changes with the temperature. Pyknometers and hydrometers are usually graduated for use at a certain temperature, and when so used no correction is necessary. These instruments frequently have thermometers attached.

Gas Density.—*Gas Density* or *Vapor Density* is the weight of a gas or vapor as compared with pure, dry air, or pure, dry hydrogen. Since changes of temperature and pressure greatly affect the volume of gases, it is always necessary to make corrections for these. For the sake of uniformity reductions are made to 0° C. temperature and 760 mm. pressure, these being what are called *standard conditions.*

Gas density is obtained by dividing the weight of a given volume of the gas by the weight of the same volume of air or hydrogen. The density referred to air is commonly called *specific gravity.* The comparison with hydrogen is more convenient for

chemical purposes. As used in this work gas density will always mean reference to hydrogen, its density being 1.

The weight of a liter of hydrogen under standard conditions is 0.08995 gram; that of a liter of air is 1.2932 grams. The specific gravity then of hydrogen is $\frac{0.08995}{1.2932} = 0.0696$. The gas density of air is $\frac{1.2932}{0.08995} = 14.38$. These then are easily interconvertible.

Specific gravity equals gas density multiplied by 0.0696.

Gas density equals specific gravity multiplied by 14.38.

Density is sometimes referred to oxygen as a standard. A liter of oxygen under standard conditions weighs 1.429 grams. Its specific gravity is 1.105. Its gas density is 16.

Determination of Gas Density.—Only an outline of the method of determining gas density can be given here. For the details the student is referred to works on Physical Chemistry. Two cases arise.

1. *The substance is a gas at the ordinary temperature.* In this case a glass globe holding about 500 cc., whose volume and weight are known, is filled with the gas and weighed. It is then filled with the standard and weighed, the conditions remaining the same. The weight of the globe is subtracted and proper reductions made and then the specific gravity obtained by dividing the first weight by the second.

2. *The substance is a liquid or solid.* In this case the determination must be made at a temperature above the boiling-point of the substance, and corrections must be made for temperature and pressure. The general formula for these corrections is

$$v = v'\left(\frac{273}{t + 273} \times \frac{h}{760}\right),$$

in which v' = the volume of the gas used;

t = the temperature of the gas when weighed;

h = the height of the barometer at the time of the experiment.

There are two methods:

a. A given volume of the vapor is weighed. Into a globe whose capacity is known is introduced enough of the substance to more than fill it when converted into vapor. The globe is immersed in a bath whose temperature is above the boiling point of the substance. As the vapor is formed the

air is expelled, and when the whole of the substance is vaporized the globe is sealed or closed with a stopcock, and the temperature of the bath and the reading of the barometer taken. The globe is allowed to cool and then weighed. This weight is equal to the weight of the globe (g) plus the weight of the vapor that fills it (s) minus the weight of the volume of air displaced by the globe (a). We have then the equation $w = g + s - a$. Transposing we have $s = w - g + a$. This weight divided by the weight of the volume of hydrogen required to fill the globe is the density. This is the method of Dumas.

b. The volume occupied by a given weight is measured. A small bottle containing a weighed quantity of the substance is introduced into a graduated barometer-tube filled with mercury and surrounded by a temperature-bath. The vapor as it is formed escapes from the bottle and displaces the mercury. When the vaporization is complete the mercury is brought to the same level without and within the tube and the volume read. The temperature and pressure are also noted. The volume is corrected to standard conditions and the density obtained in the usual way. This is the method of Gay-Lussac as improved by Hofmann.

In the method of Victor Meyer the vapor is generated in a tube containing air and the displaced air is collected in a graduated tube over water and the volume measured. The liquid B, whose boiling-point must be above that of the substance under investigation, is boiled until the temperature is uniform in the tube A. About 0.1 gram of the substance enclosed in a little bottle is dropped into the bulb C and the opening at D quickly and firmly closed with a cork. As the vapor forms, air to an equal amount is expelled through E into the graduated tube F, which is filled with water and inverted over the basin G.

Fig. 3.
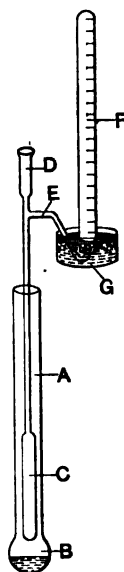
Example.— 0.12 gram alcohol yielded 62.6 cc. vapor at 17° and 750 mm. Reduced to 0° and 760 mm. this equals $62.6 \times \dfrac{273}{290} \times \dfrac{750}{760} = 58.2$ cc. 0.12 gram hydrogen equals 1339 cc., which divided by 58.2 gives 23, the gas density of alcohol.

CHAPTER IV.

PROPERTIES RELATING TO MOLECULES.—MOLECULAR PHYSICS.

HEAT.

Definition of Heat.—Heat phenomena are supposed to be due to molecular motions or vibrations. Each molecule oscillates and rotates within its space. The intensity or energy of this motion determines the temperature of the body. We distinguish *intensity* of heat and *quantity* of heat.

Intensity of Heat or Temperature.—The temperature of a body or its intensity of heat depends upon its *average molecular energy*. It must be carefully distinguished from quantity of heat, which is the total or aggregate molecular energy. Temperature is measured by an instrument called the *thermometer,* and is expressed in degrees based upon an arbitrary standard. The action depends upon the expansion and contraction of some particular substance under changes of temperature. Mercury, platinum, air, hydrogen, and other substances are used. Mercury is the most suitable for ordinary purposes and is the one in common use.
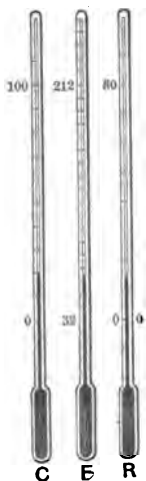
The Thermometer.—The thermometer consists of a bulb and stem made of glass and partly filled with mercury. As the mercury expands and contracts the column rises and falls in the stem. The instrument is graduated by immersing it in steam and then in melting ice and marking the respective points at which the column of mercury stands. The distance between these points is divided into one hundred equal parts, the lower point being marked 0° and the upper one 100°. The graduation is then extended up and down as far as desirable. This is the Centigrade thermometer. In the Fahrenheit ther-

FIG. 4.
THERMOMETER.

18

mometer the freezing-point is marked 32° and the boiling-point 212°. The zero is then 32° below freezing. In the Réaumur thermometer the boiling-point is marked 80°. It is not much used. Degrees below zero are written with the minus sign.

Conversion of Thermometric Readings.— Since 100° C. is equal to 180° F., 1° C. is equal to 9/5 of 1° F., and 1° F. is equal to 5/9 of 1° C. Remembering that the zero is at 32° F., the following formulas for reduction will be understood:

$$C = 5/9(F - 32); \qquad F = 9/5C + 32.$$

The Air-thermometer.—Under a constant pressure air expands and contracts with great uniformity when subjected to changes of temperature. The air-thermometer, though clumsy in form, is the best standard of reference, and is used in standardizing or testing the mercurial thermometers.

Extreme Temperatures.—Very high and very low temperatures cannot be determined with ordinary thermometers. Instruments are used in such determinations whose action depends upon various physical properties, such as the expansion of metals, the relative expansion of two metals, the change of electric resistance, etc., due to changes of temperature.

Absolute Temperature.—A gas such as air at constant pressure changes the $\frac{1}{273}$ part of its volume at 0° for every degree of change in temperature. If its temperature be raised from 0° to 273°, its volume will be doubled. If a gas could have its temperature reduced to − 273° C., its volume would theoretically become zero. Practically it becomes a liquid before this temperature is reached and the rate of volume change is altered.

If now a scale be arranged with its zero at − 273°, the volume of a gas will vary directly as its temperature on this scale. This is called *absolute zero* and readings of this scale are called *absolute temperature*. Absolute temperature is obtained by adding 273° to the ordinary centigrade readings.

Quantity of Heat.—The quantity of heat in a body is its *aggregate* or *total molecular energy*. If flames of equal intensity be used in heating equal quantities of different substances, the temperatures will rise with different degrees of rapidity. The temperature of iron will rise nearly nine times and that of mercury about thirty times as rapidly as that of water. Quantity of heat,

therefore, depends not only upon the temperature, but upon the nature of the substance itself.

Heat-unit.—The heat-unit, or *Calorie,* is the quantity of heat required to raise one kilogram of water from 4° to 5° C., or through 1°. The *gram-calorie,* or simply *calorie,* is the quantity required to raise one gram of water from 4° to 5° C.

Heat Capacity.—Specific Heat.—The quantity of heat required to raise the temperature of a body through 1° is called its *heat capacity.* The number of Calories required to raise the temperature of one kilogram of the substance from 4° to 5° C. is called its *specific heat.* Specific heat is therefore the heat capacity of a substance as compared with water. Water has a greater heat capacity, that is, heats more slowly, than any other solid or liquid substance. It is therefore a suitable standard and its specific heat is 1. All other specific heats will be fractions.

The total quantity of heat in a body in heat-units is equal to the continued product of its mass, its specific heat, and its absolute temperature.

The great difference in heat capacity is illustrated in the following table. In the first column is given the temperature through which a kilogram of the substance would be raised by the quantity of heat required to raise a kilogram of water through 1°. In the second column are the specific heats, which are the reciprocals of the numbers in the first column.

Water......1°	1.000	Iron........8.8°	0.113
Sulfur......4.9°	0.208	Silver......17.5°	0.057
Glass.......5.6°	0.177	Mercury....30.0°	0.033

Change of Specific Heat.—The specific heat varies slightly with the temperature and greatly with the physical state. The specific heat of a liquid increases with the temperature. That of water at 80° is 1.0089. Substances in liquid state have higher specific heats than in solid or gaseous state. The specific heat of ice is 0.504, and that of steam is 0.480.

Atomic Heat.—It was found by Dulong and Petit as early as the year 1819 that the specific heats of the solid elements were approximately inversely proportional to their atomic weights; or that quantities of the elements taken in proportion to their atomic weights had equal capacities for heat; or that the atomic heat capacity of all the elements in the solid state is the same. This

constant quantity which may be obtained by multiplying the specific heat by the atomic weight is called *atomic heat.* It is about 6.4. To this law, called the law of Dulong and Petit, there are some exceptions, chiefly among the non-metallic elements.

The following table illustrates the law and the exceptions:

Element.	Specific Heat.	Atomic Weight.	Atomic Heat.
Lithium.................	0.94	7	6.6
Potassium...............	0.166	89	6.5
Calcium....:............	0.170	40	6.8
Gold...................	0.082	196	6.2
Glucinum...............	0.41	9	3.7
Carbon (diamond)........	0.147	12	1.7

The exceptional elements follow the law more nearly at high temperatures. The specific heat of diamond at 900° is about 0.46, which would give an atomic heat of 5.5. So also glucinum at 500° has a specific heat of 0.62, corresponding to an atomic heat of 5.6.

Molecular Heat.—Molecular heat is obtained by multiplying the specific heat of a compound by its molecular weight. It is approximately equal to the sum of the atomic heats, and divided by the number of atoms in the molecule should give the atomic heat constant 6.4.

Atomic Heat from Molecular Heat.—The atomic heat of the gaseous elements may be determined indirectly from the molecular heat of their compounds. The specific heat of silver chloride is 0.089, its molecular weight is 143.5. Its molecular heat is therefore $0.089 \times 143.5 = 12.77$. The atomic heat of silver is 6.1. The atomic heat of solid chlorin is then $12.77 - 6.1 = 6.6$.

Specific Heat Determinations.—There are three principal methods of determining specific heat: (1) the method of the ice calorimeter, (2) the method of mixtures, (3) the time method. In the first two methods the computation is based upon the principle that the change of heat quantity is equal to the continued product of the mass, the temperature change, and the specific heat. Thus, if 20 grams of water are raised from 10° to 20°, the change of heat quantity is, since the specific heat of water is 1, $20 \times 10 \times 1 = 200$ calories. To raise the same amount of gold through 10° would re-

quire, since the specific heat of gold is 0.032, $20 \times 10 \times 0.032 = 6.4$ calories. In the third method it is assumed that the times required for equal weight of two bodies to cool through a given number of degrees are proportional to their specific heats.

Examples.—First Method. 150 grams of nickel at 500° melted 103 grams of ice at 0°. The heat of fusion of ice is 79.25 calories. If x represents the specific heat of nickel, we have $150 \times 500 \times x = 103 \times 79.25$, or $x = 0.109$.

Second Method. 100 grams of lead, after having been suspended in boiling water for ten minutes, were quickly immersed in 100 grams of water at 0° when the temperature rose to 3.3°. The water had gained $100 \times 3.3 \times 1$ calories and the lead had lost $100 \times 96.7 \times x$ calories, x being the specific heat of the lead. We have then $100 \times 96.7 \times x = 100 \times 3.3 \times 1$, or $x = 0.034$.

Third Method. 1.3 kilograms of turpentine cooled from 25° to 5° in 22.15 minutes, while the same amount of water cooled through the same number of degrees in 52 minutes. We have therefore, $52 : 22.15 :: 1 : x$, or $x = 0.426$, the specific heat of turpentine.

LIGHT.

Definition of Light.—Light is supposed to be due to vibrations in ether. Ether is the highly elastic hypothetical fluid which fills interstellar space and penetrates between the molecules and atoms of all material bodies. Light is transmitted through ether in the form of waves with a velocity of about 186,000 miles a second. Heat is also transmitted through ether, but heat as such is more properly due to molecular motion in material bodies.

The light phenomena which most concern chemists are (1) chemical effect, (2) refraction, (3) color, (4) the spectrum, and (5) polarization.

The chemical effects of light will be fully treated in photochemistry.

Refraction of Light.—When a ray of light passes from one medium to another of different density, it is refracted or bent from its course. If the second medium is denser than the first, the ray is bent toward the perpendicular to the plane joining the two media; if the second is the rarer, the ray is bent away from such perpendicular. The refraction varies as the sine of the angle which the incident ray makes with the perpendicular. The index

of refraction is the quotient arising from dividing the sine of the angle of incidence by the sine of the angle of refraction. All transparent bodies, solid, liquid, and gas, have their special refractive indices, and this constitutes one of the important physical properties of chemical compounds. The mean indices of refraction of a few substances are as follows: Diamond, 2.5; Alcohol, 1.37; Flint glass, 1.61; Water, 1.33.

Color.—White light is a mixture of rays of different wavelength. When this mixture of rays falls upon the retina of the eye it produces the sensation of whiteness, or simply lightness. If these rays are separated and allowed to fall upon the retina, they produce those various sensations which we call colors. Color is due to the absorption of certain of the light-rays and the reflection of others. A red object reflects the red rays and absorbs the others, while a blue or green object reflects only blue or green rays.

The Spectrum.—In passing through a prism the rays of light of different wave-lengths undergo different degrees of refraction. A beam of light thus spread out is called the *spectrum*. The red light is refracted least and the violet light most. Beyond the red and the violet are other rays which are colorless and invisible. These are called the ultra-red and ultra-violet rays. The former are heat-rays and the latter, having a powerful chemical effect, are called *chemical* or *actinic* rays.

The band of varying color produced by white light is called the *continuous spectrum*. If a ray of colored light be passed through a prism, the spectrum is not continuous, but consists of one or more colored lines in that portion of the spectrum which corresponds to the color of the light. The chemical elements give *discontinuous* spectra, some few and some many lines, and some give lines in quite distant portions of the spectrum, as, for example, potassium. The spectrum thus becomes the means of identifying chemical elements. The process is called *spectrum analysis* and the instrument used is called the *spectroscope.*

The Spectroscope.—The spectroscope consists essentially of a prism, *P*, for dispersing the light, a collimating-tube, *R*, with a narrow slit at one extremity and a lens at the other for admitting a thin ribbon of light to the prism, a telescope, *A*, through which the spectrum is seen magnified, and a tube, *C*, containing a scale

the image of which is reflected from the face of the prism into the telescope alongside of the spectrum.

To use the instrument, direct the collimating-tube towards a source of light, arrange a candle or light reflected from a window
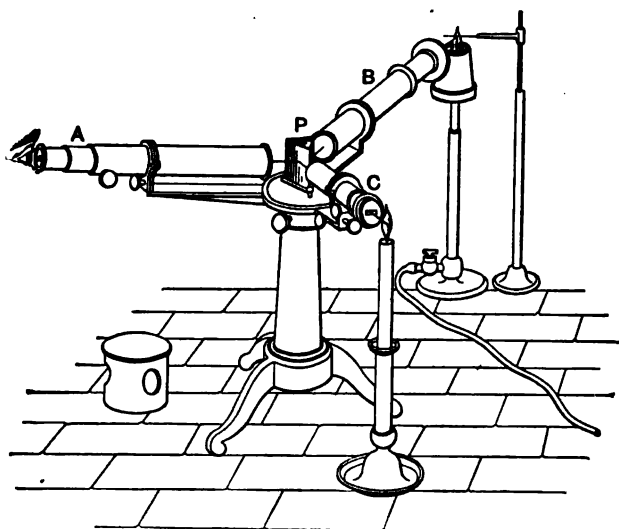

FIG. 5.—SPECTROSCOPE.

with a small mirror so as to illuminate the scale and observe the spectrum through the telescope.

Illustrations.—Direct the instrument towards a bright white light and observe the continuous spectrum. Place a colorless Bunsen flame in front of the slit, dip a platinum wire into a strong solution of common salt and hold it in the flame ; the flame becomes yellow and the spectrum is not continuous but consists of a bright yellow line. Repeat the experiment with lithium chlorid and potassium hydrate. In the first case we have two lines, one red and the other orange; in the second case there are three lines, two in the red and one in the violet. The last line is difficult to see. If a mixture of the compounds is used, all the lines will be seen at once.

Absorption Spectra—Fraunhofer Lines.—Upon close observation the solar spectrum will be seen to be crossed by a multitude of dark lines, many of which are coincident with the colored spectra of the various chemical elements. Experiment has shown that when white light is passed through the vapor of a metal before entering the spectroscope a dark line appears where the

spectrum of the metal should be. *The vapor of a metal absorbs the light which the metal itself produces* (Law of Kirchhoff). This is called the *absorption spectrum*, and the lines are called *Fraunhofer lines*, from the name of the man who first mapped them and indicated the prominent ones by the letters of the alphabet. The non-metals also give absorption spectra.

To explain the dark lines in the solar spectrum we may suppose that the sun's atmosphere is filled with incandescent vapors which

FIG. 6.—FRAUNHOFER LINES.

absorb the rays corresponding to the spectra of these vapors as the light passes out from the luminous body of the sun. To ascertain what elements are in the sun it is only necessary to identify certain Fraunhofer lines with the spectra of those elements. Among those which have been found are hydrogen, sodium, copper, zinc, magnesium, potassium, calcium, chromium, nickel, barium, strontium, cadmium, cobalt, manganese, aluminum, lead, titanium, and oxygen. The sun's chromosphere is supposed to be incandescent hydrogen. The Fraunhofer lines are exceedingly numerous and comparatively few have been referred to terrestrial elements. We may therefore suppose that the sun contains many substances which do not exist on the earth. By means of the spectroscope many known substances have been found in the fixed stars and nebulæ.

The principal Fraunhofer lines with the color, wave-length, and number of vibrations per second are given in the following table:

Line.	Color.	Wave-length in millimeters.	Number of waves per second.
A	Dark red	0.000760	395,000,000,000,000
C	Orange	0.000656	458,000,000,000,000
D	Yellow	0.000589	510,000,000,000,000
E	Green	0.000527	570,000,000,000,000
F	Green-blue	0.000486	618,000,000,000,000
G	Ultra blue	0.000431	697,000,000,000,000
H	Violet	0.000397	760,000,000,000,000

Double Refraction and Polarization.—A transparent body which is homogeneous and presents the same structure in all directions is *isotropic.* Light passing through such a body is refracted according to the law of sines. If, however, the body presents difference of structure in different directions, the ray of light is separated into two rays, only one of which follows the law. This is called the *ordinary ray,* while the other is called the *extraordinary ray,* and the action is called *double refraction.* The phenomenon is well seen with crystallized calcite or Iceland spar. A small object seen through such a crystal appears double.

Both rays of light coming from the prism are polarized. In common light-rays the ethereal vibrations are perpendicular to the line of propagation, but in no particular direction. In polarized light the vibrations are confined to a plane. It is as if the light in passing through the crystal had been so sifted as to let through only those vibrations which were parallel to the planes of crystallization. If two crystals of tourmalin cut parallel to their axes be held in similar position between the eye and a light, the light will be seen through them. If now one of the crystals be revolved in a plane parallel to its faces, the light will gradually fade and when the angle of 90° is reached will disappear. If the rotation be continued, the light reappears and at 180° has its full strength. The light in passing through the first prism is polarized in a plane and can only pass through the second prism when it has a position similar to that of the first. An apparatus consisting of two such prisms is called a *polariscope.* The prism which first receives the light is called the *polarizer,* the one next to the eye is called the *analyzer.*

A Nicol prism is a crystal of Iceland spar which has been cut and then cemented together with Canada balsam in such a way as to permit the extraordinary ray to pass through while the ordinary ray is totally reflected from the layer of balsam and passes out at the side of the prism. The common polariscope is composed of two such Nicol prisms, with graduated circles for measuring the angle of rotation, tubes for holding solutions, and various other accessories.

When polarized light is passed through solutions of certain chemical compounds, such as sugar, the plane of polarization is rotated, and the amount of rotation as determined by the polari-

scope becomes a means of determining the strength of such solutions. The instrument used for determining the strength of sugar solutions is called a *saccharimeter*.

Special Light Phenomena.—*Opalescence.*—When light enters a medium which contains fine solid particles in suspension, the shorter light-waves are more abundantly reflected than the longer ones, and hence the medium appears blue. The light coming directly through the medium is yellow. There is therefore a play of colors between blue, yellow, and white. The phenomenon is called *opalescence*. Examples are seen in dilute milk, smoky atmosphere, soapy water, opal, and the blue sky.

Phosphorescence.—The longer ethereal waves easily communicate their motion to material molecules as heat. The shorter light-waves seem to produce but little molecular motion, or rather the motion ceases as soon as the light ceases to act. There are some substances, however, in which the vibrations continue. They shine in the dark for some time after having been exposed to a strong light. Such substances are said to be *phosphorescent*. Among them are diamond, sugar, silk, and the sulfids of barium and calcium.

Fluorescence.—There are certain substances in which molecular vibrations produced by light-waves give rise to other light-waves of greater length, but not so long as heat-waves. Such substances are said to be *fluorescent*. When illuminated with white light they give out light of various colors which seems to come from within. They are even made luminous by ultra-violet rays, the shorter invisible rays being changed into longer visible rays. Among fluorescent substances are æsculin (from horse-chestnut), quinine sulfate, petroleum, uranium compounds, fluor-spar, eosin, fluorescein, and sulfids of barium and calcium. Good fluorescent solutions may be obtained by soaking horse-chestnut twigs in water, or making a dilute solution of eosin.

In some cases of fluorescence we find slower waves converted into more rapid ones. A solution of naphthalin red when acted upon with a deep red light fluoresces with an orange light. In the case of chlorophane (a variety of fluor-spar) even the slow heat-waves cause it to emit an emerald-green light.

Calorescence.—If dark heat-rays be brought to a focus on a piece of platinum, the platinum becomes luminous and emits light-

waves of all kinds. This raising of longer waves into shorter waves was called by Tyndall *calorescence.*

ELECTRICITY.

Potential.—When two bodies are in different electric conditions, they are said to be electrified and the two conditions are rather arbitrarily called *positive* and *negative.* *Potential* is the tendency of electrified bodies to discharge their electricity to other bodies or to the earth. When two bodies having different potential are connected by a conductor a current of electricity flows from that of higher or positive potential to that of lower or negative potential until there is equilibrium. The earth is the great reservoir or storehouse of electricity and its potential is said to be zero.

Sources of Electricity.—Among the many ways of generating electricity only two need be mentioned here: first by means of chemical action, as seen in the galvanic battery, and second by mechanical work as represented by the dynamo.

The Battery.—A battery-cell consists essentially of two metals immersed in a liquid which acts chemically upon one of them.
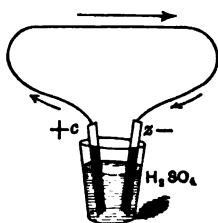
FIG. 7.

On connecting the metals with a copper wire a current of electricity passes from one to the other. Amalgamated zinc and copper (carbon or platinum) with dilute sulfuric acid make a very simple battery. The copper with its connecting wire is called the *positive pole of the battery,* or *positive electrode* or *anode;* the zinc is the *negative pole* or *negative electrode* or *cathode.* The current is said to pass from the anode to the cathode, and in electrolysis the positive element goes in the same direction. In the cell itself the zinc is positive and the copper negative and the current passes through the liquid from the former to the latter.

The Dynamo.—The dynamo consists essentially of a coil of wire revolving across a magnetic field, thus generating a current of electricity. The coil of wire is called the *armature,* and the powerful electromagnet in front of which it revolves is called the *field-magnet.* It is run by an engine and thus mechanical work is converted into electricity. The motor is the dynamo reversed; that

is, the current in the electromagnet makes the armature revolve. Thus electricity is converted into work.

Electrochemical Terms.—Many substances under various conditions, especially in solution, separate apparently into two or more parts called *ions:* the one carrying positive electricity and called *cations;* the other carrying negative electricity and called *anions.* Such substances are termed *electrolytes* because they are decomposed by the electric current. If the electrodes of a battery (leaves of platinum or other substance attached to the wires of the battery) are placed in a solution of an electrolyte, the cations will move through the solution to the cathode, while the anions will go to the anode, and both will lose the electric charge and be liberated. Such decomposition is called *electrolysis.*
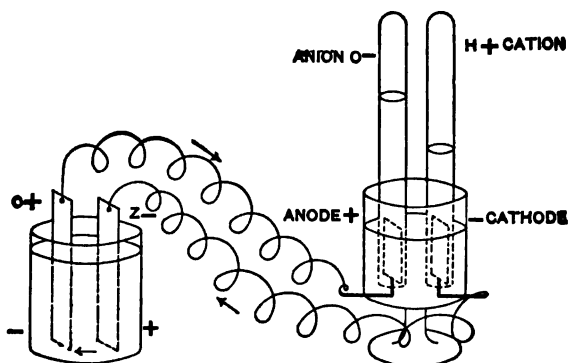
FIG. 7a.—ELECTROLYSIS OF WATER.

Electric Units.—Many units are used in electricity and they are difficult to understand. A few of them are here briefly defined.

The *coulomb*, named for a French chemist who lived in the early part of the nineteenth century, is the *unit of quantity.* It corresponds to the calorie or unit of heat and to the liter or unit of volume. It is the quantity of electricity carried by 1.118 milligrams of silver ions. For the evolution of one gram of hydrogen 96,530 coulombs of electricity must pass through the electrolyte.

The *ampere*, named for the great French chemist, is the *unit of current strength.* A current which causes one coulomb of electricity to pass a cross-section of a conductor in one second has a

current strength of one ampere. It may be compared to a stream which delivers one liter of water a second. A current of one ampere will liberate one gram of hydrogen in 96,530 seconds.

The *volt*, named for Volta, the great Italian scientist, is the *unit of pressure* or of *difference of potential*, called also *electromotive force*. It corresponds to water pressure due to difference of level. It is the pressure which will carry·an ampere current through a unit of resistance (see ohm below).

The *ohm*, named for a German electrician, is the *unit of resistance*. A difference of potential of one volt will cause a current of one ampere to pass through a resistance of one ohm. It is equal to the resistance of a column of mercury at 0° 106.3 centimeters in length, and with a uniform cross-section of one square millimeter. *The resistance in ohms is equal to the pressure in volts divided by the current in amperes.* This important relationship is known as *Ohm's Law.* The *specific resistance* of a substance is its resistance as compared with that of mercury. *Conductivity* is the reciprocal of the resistance.

The *watt*, named for James Watt, the Scotch inventor, is the unit of power. It is equal to the current in amperes multiplied by the pressure in volts. A horse-power is equal to 746 watts. A kilowatt, or 1000 watts, is about equal to one and one third horse-power. An incandescent lamp supplied by a current of one ampere at a pressure of 100 volts will give the same light as a lamp using a current of four amperes at a pressure of 25 volts.

The *joule*, named for J. P. Joule, an English physicist, is the *unit of work.* It is the work done when a coulomb of electricity is passed through a wire at a pressure of one volt, or when a current of one ampere is kept up for one second against a resistance of one ohm.

ENERGY.

Energy.—Energy may be defined as power of doing work. It is associated with matter and is a strain or stress due to state or configuration. As long as the strain is resisted or balanced, no work is done and the energy is *potential.* If the resistance yields, the state or configuration begins to change, work is done, and the energy becomes *kinetic.* The sum total of the energy potential and kinetic is constant. As a system loses potential energy it gains

an equal amount of kinetic energy and *vice versa*. The strain required to resist the transformation of potential into kinetic energy is called *force*. There are various kinds of energy: mechanical, thermal, vital, electric, radiant, etc.

No body or system can be deprived of the whole of its energy and we have no means of knowing the total energy which it may contain. The excess of its energy in any condition above that which it possesses at a standard state is called its *intrinsic energy*. This may be obtained by allowing the body or system to pass from the given state to the standard state in such a way that all the energy involved will appear and be measured in one form, say as heat.

The unit of force is the *dyne*. It is the force which acting upon one gram for one second will give it a velocity of one centimeter a second. A falling body at Paris acquires in one second a velocity of 981 centimeters (32.2 feet). Therefore *one gram-centimeter is equal to 981 dynes*.

The unit of work is called the *erg*. It is the work done when a unit of force acts through a unit of distance; that is

$$\text{Ergs} = \text{dynes} \times \text{centimeters.}$$

Energy Factors.—Energy may be expressed by two factors, one of which represents quantity and the other intensity. In mechanical kinetic energy the quantity factor is the mass and the intensity factor is the velocity. It is expressed by the equation

$$E = \tfrac{1}{2}mv^2.$$

For potential energy the factors are the spaces moved over and the force f or striving of the body or system to change state or configuration; that is,

$$E = sf.$$

For heat the factors are the heat capacity of the body or its specific heat c, and the temperature t; that is,

$$E = ct.$$

For electricity the value is

$$E = cv = \text{coulombs} \times \text{volts.}$$

In computing energy it is necessary to fix standard values for the intensity factors. Those commonly used are: for velocity, centimeters a second; for force, the dyne; for temperature, absolute zero; for electricity, the zero potential of the earth.

Chemical energy is least known of all. Its capacity factor is mass, but its energy factor has not been determined. Chemical energy must, therefore, be converted into some other form of energy before it can be measured.

In order that two systems may exist together, their intensity factors must be equal. If these are different, a change will begin and continue until the factors are the same. Thus, if two bodies at different temperatures are brought into contact, heat exchange will take place until the temperatures are equalized. If the intensity factors are the same, equilibrium will exist, whatever may be the quantity factors.

Transformation of Energy.—All the various kinds of energy are interconvertible. Mechanical motion is changed into heat in friction, into electricity in the dynamo; chemical energy is changed into electricity in the battery, into mechanical motion in the steam-engine; electricity is changed into mechanical motion in the motor and into chemical action in electrolysis. The rule has been found to hold good in so many cases that we feel safe in assuming that *any kind of energy may be transformed into any other kind of energy.* This is the *law of correlation* or *transformation of energy.*

Conservation of Energy.—The fact has been established by many satisfactory proofs that in all its transformations no energy is lost, or that the sum total of energy in the universe is constant. This is known as the *law of conservation of energy.*

Mechanical Equivalent of Heat.—Dr. Joule of England determined the mechanical equivalent of heat by noting the rise in temperature of a definite quantity of water caused by stirring it with a paddle-wheel run by a weight. The work done upon the water was measured by the distance over which the weight descended multiplied by the mass of the weight. He found that an 8-kilogram weight descending through 53 meters caused a rise in temperature of 1° in 1 kilogram of water, that is, produced one calorie of heat. To do the same work a 1-kilogram weight would have to descend 424 meters. The work done by a kilogram weight descending through 1 meter is called a *kilogrammeter.* Therefore

One calorie of heat is equivalent to 424 kilogrammeters of work.

More accurate determinations made by Henry A. Rowland of Johns Hopkins University gave the value 425.5.

Heat Equivalent of Electricity.—We have found that electric energy is represented by the equation $E = cv = $ coulombs $\times$ volts. If we measure the heat generated when a coulomb of electricity is driven through a resistance which lowers its potential by one volt, we find it to be 0.24 calorie.   Therefore

$$1 \text{ coulomb} \times 1 \text{ volt} = 0.24 \text{ calorie,}$$

or *the heat equivalent of electricity is 0.24 calorie.*

Mechanical Equivalent of Electricity.—Since one calorie of heat is equal to 42,550 gram-centimeters, and one gram-centimeter is equal to 981 dynes, we have

$$E = 0.24 \times 42{,}550 \times 981 = 10{,}017{,}972 = 10^7 \text{ ergs.}$$

The mechanical equivalent of electricity is then 10^7 ergs.

Other energy equivalents will be discussed in their proper connection.

PART II.

THEORETICAL CHEMISTRY.

DIVISION I. STATICS.

CHAPTER V.

ELEMENTS AND ATOMS.

Elements.—Analysis of all known substances has shown that they are composed of only a few ultimate kinds of matter called *elements*. Some of the elements are the common substances with which we are familiar, such as gold, iron, silver, copper, oxygen, etc. Others do not occur free and are only obtained by complicated chemical processes.

Abundance of Elements.—Some elements are very abundant in nature, while others are so rare that they are prepared at great expense and are never seen outside of chemical collections and laboratories. One half of the surface rocks of the globe and eight ninths of water are oxygen, while the element gallium is so rare that the market price is $12.00 a grain.

Number of Elements.—The number of elements now known is seventy eight. All other substances, natural or artificial, are compounds, that is contain more than one element. Any of these elements may hereafter be found to be combinations or modifications of other elements.

Naming of Elements.—The elements have been named without much regard to system. Those which have long been known usually retain their common name, as gold, silver, copper, lead,

34

mercury. In naming compounds the Latin equivalent of these is frequently used, as auric chlorid, cuprous oxid, etc. Of those elements which have been more recently discovered the name of the metals usually ends in *um*, while non-metals receive the termination *ine, on*, or *gen.* The names themselves are variously derived according to the fancy of the discoverer. They have come from the names of gods: thorium from Thor, the Norse god; from heroes of mythology: tantalum from Tantalus, titanium from Titan; from the planets: tellurium from *tellus*, the earth, selenium from *selene*, the moon, also mercury and uranium from the planets of the same name; from countries: scandium from Scandinavia, germanium from Germany; from colors: chlorin, green; iodin, violet; chromium, colored; from physical properties: barium from *barus*, heavy; from natural phenomena: iridium from Iris, the rainbow; from chemical properties: oxygen, acidmaker; nitrogen, niter-maker, hydrogen, water-maker; from various sources: silicon from *silex*, flint; calcium from *calx*, lime; phosphorus from the Greek which means *light-bearer;* helium from *helios*, the sun, etc.

Symbols.—For convenience the various elements are represented by *symbols.* These are simply abbreviations of the names of the elements. In some cases the first letter only is used; as, C for carbon, N for nitrogen, O for oxygen. If two names begin with the same letter, the symbol for the less common element is formed by adding some other letter which is prominently heard in the pronunciation of the name; as, Co for cobalt, Cl for chlorin, Br for bromin. In many cases the symbol comes from the Latin name; as, Fe for iron (*ferrum*), Au for gold (*aurum*), Cu for copper (*cuprum*).

A symbol not only represents the element, but a definite quantity of it, viz., one atom, and thus indirectly expresses the atomic weight. To indicate two or more atoms the Arabic subscript numerals are added to the symbols. Thus H_2 means two atoms of hydrogen, O_3 three atoms of oxygen, etc.

Formulas.—A formula is a group of symbols representing a molecule. H_2O is the formula for water and means that a molecule of water contains two atoms of hydrogen and one atom of oxygen.

Molecular formulas are multiplied by placing before them an

Arabic numeral or enclosing them in parentheses and writing the small subscript numeral to the right. $2CO_2$ or $(CO_2)_2$ means two molecules of carbon dioxid.

A formula represents a molecule and tells:

1. What elements enter the molecule;
2. How many atoms of each element;
3. Indirectly the molecular weight.

Fundamental Laws of Chemistry.—Certain laws have been discovered by the study of chemical facts and phenomena which are fundamental and upon which the science of chemistry is built. The more important of these laws will now be given.

1. *Law of ·Conservation of Weight.*—Careful investigations have shown that if a chemical action is brought about in an enclosed space, no change of weight occurs. *The total weight of all the substances taking part in a chemical action remains unchanged.* This law seems to be universally true, and is known as the *law of conservation of weight.* Upon it are based all quantitative chemical operations.

Illustrations.—Place in the bottom of a flask a capsule containing a bit of phosphorus, close air-tight with a cork, and weigh. Warm gently until the phosphorus ignites. When the combustion is complete, and the flask has cooled, place it again upon the balance. The weight will be found unchanged.

Place in a small flask containing a solution of silver nitrate a tube containing a solution of potassium iodid. Weigh carefully, then tilt the flask so that the solutions mix. After the action weigh again.

2. *Law of Conservation of Mass.*—Since mass is proportional to weight, the law of conservation of mass follows directly from the above law. It may be stated thus: *The total mass of any system remains the same whatever chemical change may have taken place within the system.*

3. *Laws of Conservation and Transformation of Energy.*—These laws have already been explained under the subject of Energy.

4. *Law of Constant Proportions.*—Not only has it been found that no matter is lost in a chemical reaction, but it has also been demonstrated that when two substances combine to form a third, they unite in a definite proportion by mass or weight and that this proportion is always the same however the compound may be formed. Thus, water contains 8 parts of oxygen to 1 of hydro-

gen, and common salt contains 35.45 parts of chlorin to 23 of sodium, and the elements never enter these compounds in any other proportion. This law of constant proportions has been found to hold good for all substances that have been investigated, and may be stated thus: *Every chemical compound has a constant composition and always contains its constituent elements in the same proportion by mass or weight.*

5. *Law of Multiple Proportions.*—The elements have been found to combine in more than one definite proportion. For example, there are two compounds of hydrogen with oxygen. In water the proportion is 1 to 8, and in hydrogen peroxid it is 1 to 16. The proportion of oxygen in the second is exactly twice that in the first. So also there are five compounds of nitrogen with oxygen as follows:

		N	O	or	N	O
Hyponitrous oxid,	N_2O	7 to 4	or	2×14 to 1×16
Nitrogen dioxid,	N_2O_2	7 to 8	or	2×14 to 2×16
Nitrous oxid,	N_2O_3	7 to 12	or	2×14 to 3×16
Nitrogen tetroxid,	N_2O_4	7 to 16	or	2×14 to 4×16
Nitric oxid,	N_2O_5	7 to 20	or	2×14 to 5×16

In these compounds the amount of oxygen which combines with 7 parts of nitrogen is a multiple of 4, and that which combines with 28 of nitrogen is a multiple of 16. Such facts are expressed in the *law of multiple proportions* which may be stated thus: *If two elements combine in more than one proportion, the quantities of one which combine with a given quantity of the other are simple multiples of its lowest combining quantity.*

6. *Law of Combining Weights.*—If the combining proportions of all the elements be computed with reference to a definite weight of a given element taken as the standard or unit, the numbers thus obtained are the *combining weights* or the *equivalent weights* of the elements.

All chemical combinations take place in the ratio of the combining weights or in simple multiples thereof.

Illustrations.—The hydrogen equivalent of zinc may be found with the simple apparatus shown in Fig. 7b. The apparatus being filled with water, the weighed zinc (about 0.12 gram for a 50-cc. tube) is dropped into the generator and enough sulfuric acid of specific gravity 1.18 is added to displace the water. The side tube is closed with a cork to prevent

oscillation, which might cause the loss of gas. When action ceases, water is added to carry all the gas over, and the tube of hydrogen is transferred to a cylinder of water. After a few minutes the tube is raised until the water-level is the same without and within, and the volume of the gas is read. The temperature of the water and the height of the barometer are noted, the latter being corrected for vapor tension. The gas volume, reduced to 0° and 760 mm., is multiplied by the weight of 1 cc. of hydrogen. The weight of the zinc used is divided by this product and the quotient is the hydrogen equivalent of zinc. It will be half the atomic weight, since one atom of zinc displaces two atoms of hydrogen.

Example.—0.237 gram zinc gave 90 cc. hydrogen at 17° and 741 mm. The vapor tension for 17° is 14.4 mm. Then

$$90 \times \frac{273}{290} \times \frac{726.6}{760} \times 0.0000899 = 0.00728$$

gram hydrogen.

$$\frac{0.237}{0.00728} = 32.56,$$

the hydrogen equivalent of zinc.

FIG. 7b.—HYDROGEN EQUIV-
ALENT OF ZINC.

The atomic weight of zinc is 65.4 and its true equivalent is 32.7.

Theory of Atoms.—The laws just explained were interpreted by John Dalton, an English chemist, in 1805, by what is known as the *theory of atoms.* This theory supposes that each element consists of discrete particles which have a definite weight and remain undivided in chemical actions. On this supposition, if a compound is formed between two elements, the union must take place in weights proportional to the weights of the two atoms, and hence in harmony with the law of constant proportions. If one atom of one element unites to two or more of another, then the union will be in harmony with the law of multiple proportions. The atomic theory thus fully explains these laws, and practically all the facts are in accord with this theory.

An atom may then be defined as the *ultimate particle of an element which takes part in a reaction or enters into the composition of a molecule.*

Nature of the Atom.—Of the nature of the atom we know really nothing. In 1815 William Prout, an English physician, observed

that with hydrogen as the standard many of the atomic weights are whole numbers. He therefore proposed the hypothesis that all the elements are compounds of hydrogen. This hypothesis has now been abandoned because the atomic weights have been found not to be generally multiples of one.

In 1867 Lord Kelvin, an English physicist, suggested that atoms may be vortex rings in ether similar to the rings made by hydrogen phosphid, or those which come from the smoke-stack of a locomotive. This hypothesis was investigated by Lord Kelvin himself, by Clerk Maxwell, and by J. J. Thomson, and for a time received popular favor. In 1900 Professor J. J. Thomson of Cambridge, in the investigation of the cathode rays, came to the conclusion that they were streams of material particles charged with negative electricity and moving with velocities somewhat less than that of light. These particles, or *corpuscles*, as he called them, he found by electric measurement to be about seven hundred times as light as the hydrogen atom. He suggested, therefore, that atoms are clusters of hundreds and perhaps thousands of ultimate particles which are all alike. This hypothesis is in harmony with the recent discoveries in connection with radium and radioactivity, and it is probable that the atom will be found to be a complex aggregate of one or more ultimate substances.

Atomic Weight.—The smallest relative quantity of an element which enters into the composition of a molecule is called its *atomic weight*. Hydrogen, being the lightest substance, has usually been taken as the standard with an atomic weight 1. With this standard atomic weight means so many times as heavy as the hydrogen atom. Oxygen is also used as the standard, and is preferred by many chemists for three reasons:

(1) Its atomic weight being larger, the error in the determination of atomic weights is less than when the smaller standard is used.

(2) The atomic weights of many elements may be determined directly with reference to oxygen, while with hydrogen as the standard most of the determinations are indirect.

(3) The atomic weights computed with reference to oxygen more nearly approximate whole numbers. This will be seen by an inspection of the table, in which the weights are given with reference to both standards.

The most painstaking and elaborate determinations of the combining weights of oxygen and hydrogen were made by Professor E. W. Morley and published in 1895. He obtained for $H = 1$, $O = 15.879$; for $O = 16$, $H = 1.0076$.

These numbers furnish the basis for the computation of all the atomic weights.

Determination of Atomic Weight.—If the element unites atom to atom with hydrogen, an analysis of the compound will give its atomic weight.

Example.—Hydrochloric acid contains one atom each of hydrogen and chlorin. Analysis shows that it contains 2.75 per cent of hydrogen and 97.25 per cent of chlorin. These numbers are in the proportion of 1 to 35.4; therefore the atomic weight of chlorin is 35.4.

If the element does not combine with hydrogen, its atomic weight is determined by ascertaining in what proportion it combines with an element which does form a hydrogen compound.

Example.—Sodium does not combine with hydrogen, but forms with chlorin the compound NaCl, called common salt. Analysis of this compound shows 39.39 per cent of sodium and 60.61 per cent of chlorin. The atomic weight of chlorin being 35.4, the proportion $60.61 : 39.39 = 35.4 : x$, gives $x = 23$, the atomic weight of sodium.

But the element may combine with two or more atoms of hydrogen or in two or more proportions with it. In this case several combining weights may be obtained and it will not be possible to say which is the atomic weight.

Example.—Hydrogen forms two compounds with oxygen: water, H_2O, and hydrogen peroxid, H_2O_2. In the first, $H = 11.11$ per cent and $O = 88.89$ per cent, or 1 of H to 8 of O. In the second, $H = 5.88$ per cent, while $O = 92.12$ per cent, or 1 of H to 16 of O. Whether the atomic weight of oxygen is 8 or 16 must be determined by other means.

Aids in Determining Atomic Weight.—1. *Density.* There are various methods of ascertaining which of the combining weights of an element is its atomic weight. The most important of these is founded on the relationship between the vapor density of a compound and its molecular weight. According to the law of Avogadro, the molecular weight of any substance which can be volatilized without decomposition is just twice its density referred to hydrogen. Knowing the percentage composition and the molec-

ular weight of a compound, the actual quantity of each constituent in the molecule is known. This is determined for all compounds of each element, and the smallest quantity of each is called its atomic weight.

Suppose we are seeking the atomic weight of oxygen. We analyze and determine the density of a number of compounds. The results may be arranged as follows:

Com-pound.	Per Cent.		Ratio.	Density	Mol. Wt.	Molecular Ratio.	For-mula.
With H	H = 11.11	O = 88.89	H : O :: 1 : 8	9	18	H : O :: 2 : 16	H_2O
With C	C = 26.36	O = 73.64	C : O :: 3 : 8	22	44	C : O :: 12 : 32	CO_2
With S	S = 40.00	O = 60.00	S : O :: 2 : 3	40	80	S : O :: 32 : 48	SO_3
With N	N = 36.82	O = 63.18	N : O :: 7 : 12	38	76	N : O :: 28 : 48	N_2O_3

We find that oxygen enters these molecules with the weights 16, 32, and 48. In no compound is it ever found to be less than 16. Its atomic weight is therefore 16.

The same results enable us to write the formulas and to indicate the number of atoms of each element in the molecule. In the first compound we have 2 parts of H, but since the atomic weight of H is 1, this must represent two atoms and so we write H_2O. In the second there are 32 parts of O, but since its atomic weight is 16, we write CO_2. In the fourth we have 28 parts of N and 48 parts of O; therefore, since the atomic weight of N is 14 and of O is 16, we write N_2O_3.

2. *Specific Heat.* Another aid in determining atomic weight is specific heat. We have learned that the specific heat of the elements varies inversely as the atomic weight, and that there is a constant atomic heat equal to the product of the specific heat and atomic weight represented by the number 6.4. If, therefore, the specific heat of an element be determined and the number 6.4 be divided by it, the quotient will be the atomic weight. For example, the specific heat of potassium is 0.166, which is contained in 6.4 thirty-nine times, and this is the atomic weight of potassium.

While this is not a method for the accurate determination of atomic weights, it serves to indicate which one of several combining weights is the atomic weight, and is very useful with elements whose vapor density cannot be determined.

Since molecular heat is equal to the sum of the atomic heats, we may confirm atomic weights by a study of the specific heat of compounds. The molecular heat of a compound divided by the number of its atoms is equal to the atomic-heat constant, 6.4.

Example.—Calcium and chlorin combine in the proportion of 20 to 35.4. The specific heat of the compound is 0.164. If the formula is CaCl, the molecular weight is 55.4; if it is CaCl$_2$, the molecular weight is 110.8. We will then have:

For CaCl, $\dfrac{0.164 \times 55.4}{2} = 4.5$. For CaCl$_2$, $\dfrac{0.164 \times 110.8}{3} = 6.1$.

Since the latter is nearer to the constant, 6.4, we must conclude that the second formula is correct and that the atomic weight of calcium is 40.

3. *Isomorphism.* In 1819 Eilhard Mitscherlich of Berlin discovered the fact that isomorphous substances have generally analogous composition, or that the number of atoms of the corresponding elements in the two molecules is the same. Sodium chlorid, sodium bromid, and sodium iodid are analogous in composition, and have the same crystalline form, the cube. So also potassium perchlorate, KClO$_4$, and potassium permanganate, KMnO$_4$, both crystallize in rhombic prisms. If, for example, the atomic weight of iodin were unknown, and we have found sodium iodid, NaI, to be isomorphous with sodium chlorid, NaCl, we may write its formula NaI, and since it contains 127 parts of iodin to 23 parts of sodium, we may safely conclude that 127 is the atomic weight of iodin.

Valence of Elements.—The valence of an element is its combining power by number of atoms. Chlorin unites with one atom of hydrogen, oxygen with two, nitrogen with three, and carbon with four.

HCl   H$_2$O   H$_3$N   H$_4$C
Hydrochloric acid. Water.   Ammonia.   Marsh-gas.

In number of hydrogen atoms chlorin has a combining power of one, oxygen of two, nitrogen of three, and carbon of four. The valence of these elements is therefore one, two, three, and four respectively.

Many elements do not combine with hydrogen. The valence in this case is found by studying their compounds with some element which does unite with hydrogen. With chlorin, whose valence with hydrogen has just been found to be one, we have the following compounds:

NaCl   CaCl$_2$ BCl$_3$ CCl$_4$ PCl$_5$ WCl$_6$

in which the number of chlorin atoms indicates the valence of the other element.   The highest valence with which any element has been found to act is eight.

With reference to valence, elements are called monads, dyads, triads, tetrads, pentads, hexads, heptads, and octads.   These words are nouns and the corresponding adjectives are univalent, bivalent, trivalent, quadrivalent, quinquivalent, sexivalent, septivalent, and octivalent.   (Accent on the penult.)

Valence is indicated by accents or Roman numerals written to the right and above the symbol: thus, Cl^I, O^{II}, N^{III}, C^{IV}, P^V, S^{VI}.   It is indicated graphically by lines radiating from the symbol; thus,

$$Cl- \quad -O- \quad -\overset{|}{N}- \quad -\overset{|}{\underset{|}{C}}- \quad {>}P{<} \quad {>}\overset{|}{\underset{|}{S}}{<}$$
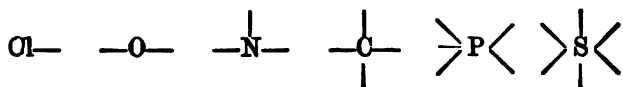
These lines represent the bonds or points of attraction by which the atoms are held together in the molecule, and in molecular formulas must all be satisfied.   Oxygen has two points and hydrogen one, and hence the formula is H—O—H.

Change of Valence.—An element does not always act with the same valence.   There are two compounds of phosphorus with chlorin, PCl_3 and PCl_5.   In the first the valence of the phosphorus is three, and in the second it is five.   So there are two oxids of sulfur, SO_2 and SO_3.   In the first the valence of sulfur is four, and in the second it is six.   Some elements have but one valence. Note the following examples:

Hydrogen	I	Oxygen	II
Gold	I, III	Calcium	II, IV
Nitrogen	I, III, V	Sulfur	II, IV, VI
Chlorin	I, III, V, VII		

Observe that in each case the valence changes by twos.   This is the general rule, to which there seem to be exceptions.   Nitrogen, for example, apparently acts with valences I, II, III, IV, and V, in the compounds N_2O, N_2O_2, N_2O_3, N_2O_4, N_2O_5.   The second and fourth formulas can be so explained as to bring them under the rule, as we shall see later.

Elements with odd valence are called *perissads*, and those with even valence are called *artiads*.

Table of Elements.—The accompanying table of elements gives the name, symbol, valence, and atomic weight with reference to both hydrogen and oxygen according to the latest official list of the International Committee on Atomic Weights (1904).

TABLE OF ELEMENTS.

NAME, SYMBOL, VALENCE, AND ATOMIC WEIGHT.

Name.	Sym-bol.	Valence.	Atomic Weight.		Approx. Weight.
			H = 1	O = 16	
Aluminum.	Al	III	26.9	27.1	27
Antimony (Stibium). . . .	Sb	III, V	119.3	120.2	120
Argon.	A	0	39.6	39.9	40
Arsenic.	As	III, V	74.4	75.0	75
Barium	Ba	II, IV	136.4	137.4	137
Bismuth.	Bi	III, V	205.9	208.5	208
Boron.	B	III	10.9	11.0	11
Bromin.	Br	I, (III, V, VII)	79.36	79.96	80
Cadmium.	Cd	II	111.6	112.4	112
Cæsium.	Cs	I	131.9	132.9	133
Calcium.	Ca	II	39.8	40.1	40
Carbon.	C	IV, (II)	11.9	12.0	12
Cerium.	Ce	IV	139.2	140.25	140
Chlorin.	Cl	I, (III, V, VII)	35.18	35.45	35.5
Chromium.	Cr	II, III, IV, VI	51.7	52.1	52
Cobalt	Co	II, IV	58.56	59.0	59
Columbium (Niobium) . .	Cb	III, V	93.2	94.0	94
Copper (Cuprum).	Cu	II, I	63.1	63.6	63.6
Erbium.	Er	III	164.8	166.0	166
Fluorin.	F	I	18.9	19.05	19
Gadolinium.	Gd	I, III	155.0	156.0	156
Gallium.	Ga	III	69.5	70.0	70
Germanium.	Ge	IV, II	71.9	72.5	72.5
Glucinum (Beryllium). . .	Gl	II	9.03	9.1	9
Gold (Aurum).	Au	I III	195.7	197.2	197
Helium.	He	0	4.0	4.0	4
Hydrogen.	H	I	1.0	1.008	1
Indium.	In	III	113.1	114.0	114
Iodin.	I	I, III, V, VII	125.9	126.85	127
Iridium.	Ir	II, III, IV	191.5	193.0	193
Iron (Ferrum)	Fe	II, III, IV	55.5	55.9	56
Krypton	Kr	0	81.2	81.8	82
Lanthanum.	La	III	137.9	138.9	139
Lead (Plumbum).	Pb	II, IV	205.35	206.9	207
Lithium.	Li	I	6.98	7.03	7
Magnesium.	Mg	II	24.18	24.36	24
Manganese.	Mn	II, IV, (VII)	54.6	55.0	55
Mercury (Hydrargyrum).	Hg	II, (I)	198.5	200.0	200
Molybdenum.	Mo	II, III, IV, VI	95.3	96.0	96
Neodymium.	Nd	III	142.5	143.6	143.6
Neon.	Ne	0	19.9	20.0	20

TABLE OF ELEMENTS—(*Continued*).

Name.	Symbol.	Valence.	Atomic Weight. H = 1	Atomic Weight. O = 16	Approx. Weight.
Nickel	Ni	II, IV	58.3	58.7	**59**
Nitrogen...............	N	III, I, V	13.93	14.04	**14**
Osmium................	Os	II, III, IV, VI, VIII	189.6	191.0	**191**
Oxygen.................	O	II	15.879	16.0	**16**
Palladium..............	Pd	II, IV	105.7	106.5	**107**
Phosphorus.............	P	III, V	30.77	31.0	**31**
Platinum...............	Pt	II, IV	193.3	194.8	**195**
Potassium (Kalium)....	K	I	38.86	39.15	**39**
Praseodymium.........	P	III	139.4	140.5	**140**
Radium................	Ra	II	223.3	225.0	**225**
Rhodium...............	Rh	III	102.2	103.0	**103**
Rubidium..............	Rb	I	84.8	85.4	**85**
Ruthenium.............	Ru	II, III, IV	100.9	101.7	**101.7**
Samarium..............	Sm	III	148.9	150.0	**150**
Scandium	Sc	III	43.8	44.1	**44**
Selenium..............	Se	II, IV, VI	78.6	79.2	**79**
Silicon................	Si	IV	28.2	28.4	**28.4**
Silver (Argentum)......	Ag	I	107.12	107.93	**108**
Sodium (Natrium)......	Na	I	22.88	23.05	**23**
Strontium.............	Sr	II	86.94	87.6	**87.6**
Sulfur.................	S	II, IV, VI	31.83	32.07	**32**
Tantalum	Ta	V	181.6	183.0	**183**
Tellurium	Te	II, IV, VI	126.6	127.6	**127.6**
Terbium...............	Tb	V	158.8	160.0	**160**
Thallium..............	Tl	I, III	202.6	204.1	**204**
Thorium	Th	IV, II	230.8	232.5	**232**
Thulium...............	Tu	I	169.7	171.0	**171**
Tin (Stannum).........	Sn	II, IV	118.1	119.0	**119**
Titanium..............	Ti	IV	47.7	48.1	**48**
Tungsten (Wolfram)....	W	II, IV, VI	182.6	184.0	**184**
Uranium...............	U	IV, VI	236.7	238.5	**238.5**
Vanadium..............	V	V, I, III	50.8	51.2	**51**
Xenon.................	Xe	0	127.0	128.0	**128**
Ytterbium.............	Yb	III	171.7	173.0	**173**
Yttrium...............	Y	III	88.3	89.0	**89**
Zinc..................	Zn	II	64.9	65.4	**65.4**
Zirconium.	Zr	IV	89.9	90.6	**90**

CHAPTER VI.

CLASSIFICATION OF THE ELEMENTS.

THE elements may be variously classified as follows:
1. Metals and Non-metals.
2. Positive elements and Negative elements.
3. Basic elements and Acidic elements.
4. Periodic arrangement of the elements.

The first three furnish practically the same classification. The metals are electro-positive and their hydroxids are bases; the non-metals are electro-negative and their hydroxids are acids. The first is the classification which has usually been adopted as the basis for treatment of the elements in the chemical text-books. The second and third are not well adapted for this purpose, since an element may be at one time positive and at another time negative, and since many elements are both basic and acidic. In the fourth the elements fall into natural groups which furnish an excellent basis for systematic and exhaustive study and treatment.

Metals and Non-metals.—The metals possess properties, mainly physical, which are known as metallic. They are solids (with the exception of mercury), are heavy, melt at high temperatures, and have metallic lustre. The non-metals are destitute of metallic lustre, five of them are gases, one is a liquid, the others are solids, some easily, others difficultly, fusible.

The line of demarkation between the metals and non-metals is not definite. Several of the elements partake of the nature of both and are called *metalloids*.

46

Positive Elements and Negative Elements.—The electric quality of an element is somewhat dependent upon the other elements with which it may be united. When the negative elements combine with one another one must assume a positive quality. Nearly all the elements, however, have such decided electric quality that they may be characterized as *positive elements* or *negative elements*. The line in the periodic table between the metals and the non-metals also separates the positive from the negative elements. Elements near this line have both qualities, being sometimes positive and sometimes negative.

Basic Elements and Acidic Elements.—When united to oxygen and hydrogen, basic elements form bases and acidic elements form acids. Basic elements are positive and metallic, while acidic elements are negative and non-metallic.

Periodic Classification of the Elements.—The law of periodicity of the elements was discovered independently by Newlands of England in 1863, Mendeleeff of Russia in 1869, and Lothar Meyer of Germany in 1869. The law may be stated thus:

The properties of the elements are periodic functions of their atomic weights.

One thing is a function of another when a change in the former produces a corresponding change in the latter. For example, carbon is a tetrad with atomic weight 12, nitrogen is a triad with atomic weight 14; a change of two in atomic weight has produced a change of one in valence. Lithium with atomic weight 7 is positive, oxygen with atomic weight 16 is negative; the addition of 9 to the atomic weight has changed the electric quality from positive to negative.

Periodicity implies a variable which returns at regular intervals through similar phases. As the atomic weight varies the properties go through a series of changes in passing from one element to another which repeats itself at pretty regular intervals. Arranging the elements in the order of the atomic weights and taking the first seven, omitting hydrogen and helium, we observe the following facts:

1. The electric quality varies from extremely positive to extremely negative.

2. The valence increases regularly to four and then decreases back to one.

3. The chemical activity diminishes, then increases.

4. The difference between two successive atomic weights is about two.

Taking the next seven elements, we observe the same gradation of properties with this additional remarkable fact, that the properties are repeated in the same order in such a way that the eighth element closely resembles the first, the ninth the second, the tenth the third, and so on through the series. In the second series the difference in successive atomic weights is alternately one and three.

The next seven elements exhibit the same gradation of properties and fall regularly into their places. Here the difference between successive atomic weights is not quite so regular.

All this is made plain by the following table. The elements in the horizontal line constitute a series, those in the vertical columns are called groups.

Valence.	I.	II.	III.	IV.	III.	II.	I.
Series 1........	Li = 7	Gl = 9	B = 11	C = 12	N = 14	O = 16	F =19
Series 2........	Na = 23	Mg= 24	Al = 27	Si = 28	P = 31	S = 32	Cl =35.4
Series 3	K = 29	Ca = 40	Sc = 44	Ti = 48	V = 51	Cr = 52	Mn=55

Observe also that the atomic weights in Series 2 are almost the exact mean of those between which they stand in both series and group.

In Series 3 potassium and calcium fall in the proper place, but chromium and manganese present properties which are quite different from those of the groups in which they fall. Furthermore, manganese is followed by three elements, iron, nickel, and cobalt, neither of which belongs to Group I. The next element, copper, has some resemblance to Group I, while selenium and bromin fall properly in Groups VI and VII. It is evident that Series 3 and 4 follow a different law from Series 1 and 2; but since they return into Group VII with bromin typical of that group, these two series are taken together to constitute a long period, and iron, nickel, and cobalt are placed in an eighth group.

The remaining elements arrange themselves in similar long periods. This is all fully exhibited in the accompanying periodic table.

PERIODIC TABLE OF CHEMICAL ELEMENTS.

Groups.	I A	I B	II A	II B	III A	III B	IV A	IV B	V A	V B	VI A	VI B	VII A	VII B	VIII A	VIII B
First short period — Ser. 1 / Ser. 2	H = 1 / Li = 7		Gl = 9		B = 11		C = 12		N = 14		O = 16		F = 19			He = 4 / Ne = 20
Second short period — Ser. 3	Na = 23		Mg = 24		Al = 27		Si = 28		P = 31		S = 32		Cl = 35.4			Ar = 40
First long period — Ser. 4 / Ser. 5	K = 39	Cu = 63	Ca = 40	Zn = 65	Sc = 44	Ga = 70	Ti = 48	Ge = 72	V = 51	As = 75	Cr = 52	Se = 79	Mn = 55	Br = 80	Fe = 56, Ni = 59, Co = 59	Kr = 82
Second long period — Ser. 6 / Ser. 7	Rb = 85	Ag = 108	Sr = 87.6	Cd = 112	Yt = 89	In = 114	Zr = 90	Sn = 118	Cb = 94	Sb = 120	Mo = 96	Te = 127	—	I = 127	Ru = 104, Ro = 106, Pd = 107	Xe = 128
Third long period — Ser. 8 / Ser. 9	Cs = 133 / Gd = 157	—	Ba = 137	—	La = 138	Tb = 160	Ce = 139		Pe = 140 / Er = 166		Nd = 143	—	Sa = 150 / Tu = 170		— —	—
Fourth long period — Ser. 10 / Ser. 11	—	Au = 197	—	Hg = 200	Yb = 173	Tl = 204	—	Pb = 207	Ta = 183	Bi = 208	W = 184		—		Os = 191, Ir = 193, Pt = 195	—
Fifth long period — Ser. 12 / Ser. 13	—	—	—	—	—		Th = 232		—		U = 239		—		— —	—
Oxide / Hydride	R₂O		R₂O₂		R₂O₃		R₂O₄ / RH₄		R₂O₅ / RH₃		R₂O₆ / RH₂		R₂O₇ / RH₁		R₂O₈	
Valence	I		II		III		IV		V / III		VI / II		VII / I		VIII / 0	

The heavy line separates the acidic from the basic elements. Elements near the line are generally acidic in the higher and basic in the lower valence.

In this table the recently discovered gases are placed provisionally in Group VIII, where they alternate with the transition elements and fit in quite well. They constitute Sub-group VIII **B** with a valence 0.

The numerous blanks represent elements not yet discovered, whose properties should be indicated by their position in the table. When the periodic law was discovered there were three blanks in the first long period, now filled by scandium, gallium, and germanium. Mendeleeff named these hypothetical elements *eka-boron*, *eka-aluminum*, and *eka-silicon* (*eka* is Sanscrit for one), and predicted the properties which they should possess. Gallium was discovered in 1875 by Lecoq de Boisbaudran, scandium by Nilson in 1879, and germanium by Winkler in 1886, and these three elements were found to have almost exactly the properties predicted for them.

Discussion of the Periodic Table.—A study of the properties of the elements, only a few of which are directly shown in the table, reveals many curious and interesting facts.

1. The atomic weights increase with regularity, each one being approximately a mean between the two adjacent ones in both group and series.

2. The valence of the groups as indicated by the oxygen compounds runs from one to eight. After passing Group IV the valence as indicated by the hydrogen compounds diminishes back to one in Group VII, and 0 in Group VIII. The elements which exhibit two or more valences are mainly in Groups V, VI, VII, and VIII.

3. The greatest chemical activity is at the beginning and end of the series, the less active elements being in the middle of the table or in Group VIII. The activity diminishes as the atomic weight increases in the negative sub-groups, and *vice versa* in the positive sub-groups. The odd series are less active than the even series.

4. In electric quality each series begins positive and ends negative, the quality being less marked with the intermediate elements. In the groups the elements become more positive as the atomic weight increases. In the long periods the even series are more positive than the odd series.

5. Each group contains a sub-group composed of the elements of the odd series which differ materially from the other members of
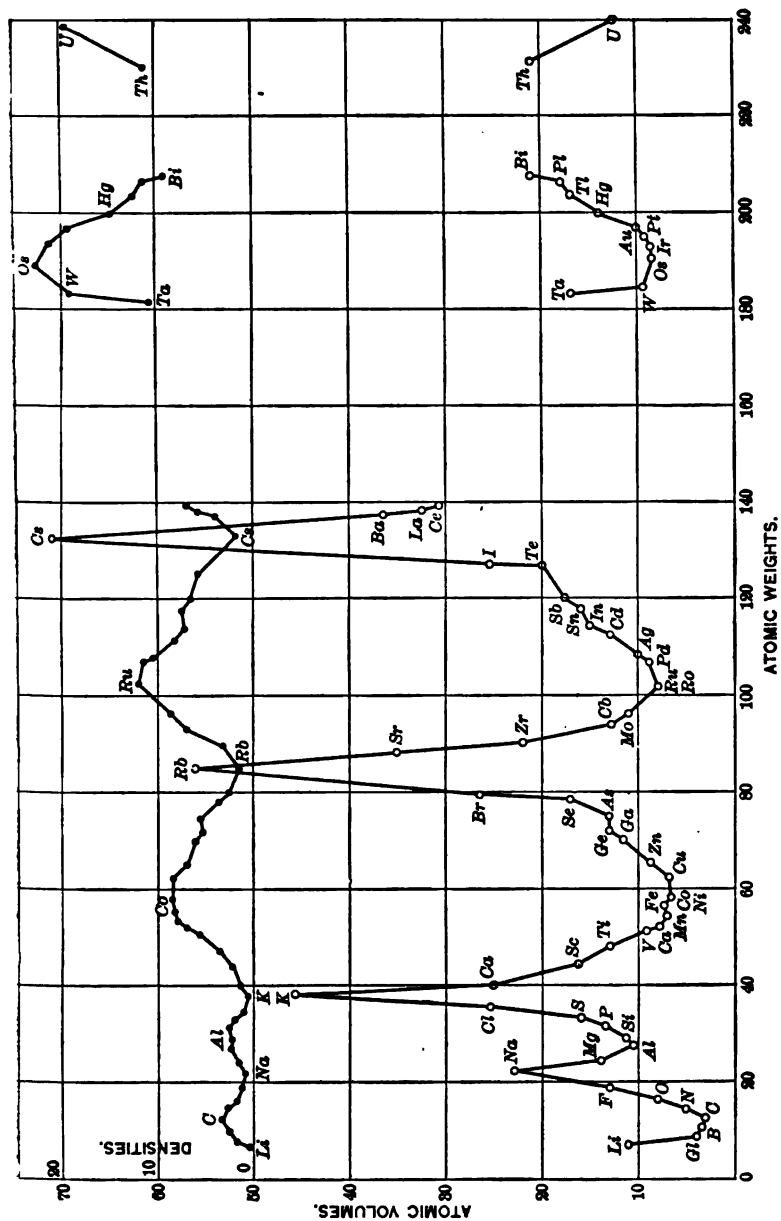
DIAGRAM OF DENSITIES AND ATOMIC VOLUMES.

ATOMIC WEIGHTS.

ATOMIC VOLUMES.

DENSITIES.

the group. These are more negative, form easily reducible oxids, and are more typically metallic in character.

6. The negative elements are gathered at the upper right-hand corner of the table. A line drawn from boron to tungsten, as shown in the table, separates the positive from the negative elements, the metals from the non-metals.

Density and Atomic Volume.—The periodicity is seen in various other properties, such as density or specific gravity, atomic volume, melting-point, malleability, ductility, volatility, etc. In none, however, is it more marked than in density and atomic volume.

The atomic volume is the quotient obtained by dividing the atomic weight by the density. This means that a number of grams of an element equal to its atomic weight occupies a number of cubic centimeters equal to its atomic volume. For example, the atomic weight of gold is 197, its density is 19.3, and its atomic volume 10.1. Therefore 197 grams of gold occupy 10.1 cc. The periodicity of density and atomic volume are well shown in the accompanying diagram. Note that as one goes up the other goes down.

Examining the diagram of atomic volumes, we observe the following facts:

1. The alkali metals, lithium, sodium, potassium, rubidium, and cæsium are at the highest points of the curve.

2. The metals of Group VIII are at the lowest points of the long periods.

3. The positive elements are on the descending and the negative ones on the ascending arms of the curve.

4. The gaseous, volatile, and easily fusible elements are on the ascending portions, while the non-volatile, difficultly fusible ones are on the descending portions or near the lowest points.

5. Some of the properties, such as malleability and electric quality, change twice in the long periods. In the first long period we have K and Ca malleable, V, Cr, Mn brittle. Fe, Cu, Zn malleable, then As and Se brittle. So also in the first and second long periods Cr and Mo are negative, though on the descending arm.

Normal and Acidic Valence.— By reference to the periodic table it will be seen that, in passing from group to group, valence rises to 4, then continues to rise to 8 or falls to 0. This may be illustrated by the following diagram.

Elements of the first four groups rarely act with any other valence than that corresponding to the number of the group. In Groups V, VI, VII, and VIII the more common valence and the one which always occurs when the element acts as the negative in binary compounds is the lower one. The series, therefore, 1, 2, 3, 4, 3, 2, 1, 0, may be called the *normal valence*. The last belongs only to the gases in Group VIII B.

In the last six groups the highest valence is the one with which the most common and most stable acid is formed. We may call this, therefore, the *acidic valence*, and it corresponds to the number of the group. Acids, and also binary compounds containing these elements acting as positives, are formed with ʼall valences between the normal and the acidic.

Defects of the Periodic System.—While the periodic law was one of the most important discoveries in chemistry and to-day furnishes the best and most scientific classification of the elements, it must be noted that the system is by no means perfect. The fact that copper, silver, and gold have so few properties in common with the alkali metals has been regarded by some as a fatal defect. If we observe, however, that each group presents similar discrepancies we may conclude that this variation is a part of the system and not a defect. In manganese we have an element which has few resemblances to the halogens; tellurium has an atomic weight too large for the place where its chemical affinities show it to belong; hydrogen, one of the most important of the elements, finds no suitable resting place; and the helioids fit but poorly into the scheme. The system, however, satisfies and explains such a multitude of facts that we may well conclude that the apparent defects are really due to our imperfect knowledge of the atomic weights and properties of the elements, and that with due modification it will be found to represent truly a great law of nature.

CHAPTER VII.

MOLECULES AND COMPOUNDS.

Theory of Molecules.—The conduct of gases, the action of liquid films, and many phenomena of light and electricity lead to the theory that matter is not continuous, but is composed of discrete particles which remain undivided as long as the substance retains its identity. These particles are called *molecules*. This theory harmonizes well with chemical facts and is generally accepted. The molecule is composed of the still smaller particles called atoms, which are held together by a force called *chemical affinity, chemical attraction*, or *chemism*. According to the laws of combination by weight, the molecule must contain a definite number of atoms of each kind, and the weight of the molecule will be equal to the sum of the weights of its atoms. To obtain this molecular weight we must know how many atoms of each element enters the molecule.

Law of Combination by Volume.—In 1808 Joseph Louis Gay-Lussac, a French chemist, discovered the law that *gases combine chemically in simple proportions by volume and that the resulting volume bears a simple proportion to the original volume.* This is known as the *law of Gay-Lussac.* For example, hydrogen and chlorin combine volume to volume to make two volumes of hydrogen chlorid; hydrogen and oxygen combine two volumes of the first to one of the second to make two volumes of steam; and three volumes of hydrogen combine with one volume of nitrogen to make two volumes of ammonia.

Hypothesis or Law of Avogadro.—In order to explain the law of Gay-Lussac, Amadeo Avogadro, an Italian physicist, in 1811, and André Marie Ampère, a French physicist, independently in 1812 proposed the hypothesis that *equal volumes of all gases at the same temperature and under the same pressure contain the same number of molecules,* or that *all gaseous molecules under like conditions are of the same size.* This hypothesis, commonly called the *law of Avogadro* or *of Ampère*, is supported by so many facts and

54

has been so helpful to chemists that it is generally recognized as an established law or theory. It enables us to determine (1) the molecular weight and (2) the number of atoms in the molecule.

1. If equal volumes of two gases contain the same number of molecules, the molecular weights of the gases will be proportional to the weights of the equal volumes, or to the densities of the gases. If m and m' are the molecular weights and d and d' the densities of the two gases, then

$$m:m'::d:d', \quad \text{or} \quad \frac{m}{d}=\frac{m'}{d'}=\text{a constant.}$$

For hydrogen $d'=1$ and $m'=2$, as shown below, and therefore

$$\frac{m}{d}=\frac{2}{1}=2, \quad \text{or} \quad m=2d, \quad \text{and} \quad d=\frac{m}{2}.$$

That is, *the molecular weight of any substance is equal to twice its gas density referred to hydrogen, and conversely the gas density is equal to half the molecular weight.*

If the substance dissociates at the temperature of the experiment, the density obtained will be intermediate between the densities of the substance and of the parts into which it dissociates. The true density may then be obtained by ascertaining the degree of dissociation and making proper computation; or by securing complete dissociation and determining the density of the parts separately.

2. One volume of hydrogen combines with one volume of chlorin to make two volumes of hydrogen chlorid, or one molecule combines with one molecule to make two molecules. Since the two molecules of hydrogen chlorid contain each one atom of hydrogen, the molecule of hydrogen must have contained two atoms, and for like reason the molecule of chlorin must have contained two atoms. This is fully expressed in the following equation:

$$H_2 \ + \ Cl_2 \ = 2HCl.$$
$$2 \text{ vols.} + 2 \text{ vols.} = 4 \text{ vols.}$$
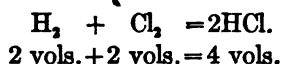
The molecules of hydrogen and chlorin are therefore diatomic and the molecular weight of hydrogen is 2.

If the hydrogen atom be taken as the unit, the volume of the hydrogen molecule will be 2, and since all molecules are of the same size, the molecular volume of any substance in the gaseous state and under standard conditions will be 2.

Elemental Molecules.—An elemental molecule is one which contains only one kind of atoms. Atoms do not readily exist free, but tend always to unite to form molecules, even though they be like. There will therefore be at least as many kinds of elemental molecules as there are elements. There are actually more, because some of the elements form molecules sometimes with one and sometimes with another number of atoms. Ordinary oxygen, for example, has two atoms in the molecule, O_2, while in the form of ozone it has three, O_3.

The *atomicity* of the elemental molecule, i.e., the number of atoms it contains, has been experimentally determined for some twenty-five of the elements. The prevailing number among the metals is one and among the non-metals two. The atomicity is somewhat dependent upon the temperature. Sulfur, for example, at 500° is hexatomic, while above 800° it is diatomic.

The atomicity of elemental molecules so far as it has been experimentally determined is as follows:

Monatomic.—Sodium, potassium, zinc, cadmium, mercury, iodin (at about 1500°), bromin (at about 1800°), bismuth, helium, argon, neon, krypton, xenon.

Diatomic.—Hydrogen, chlorin, bromin, iodin (200° to about 1000°), oxygen, sulfur (above 800°), selenium (above 1200°), tellurium, nitrogen, phosphorus (at white heat), arsenic (at white heat), thallium (at 1730°).

Triatomic.—Oxygen as ozone, selenium (at 800°).

Tetratomic.—Phosphorus, arsenic (at near white heat).

Hexatomic.—Sulfur (at 500°).

Octatomic.—Sulfur (at 173° and under 2 mm. pressure).

The names of elemental molecules are the same as the names of the elements. They are written by indicating in the usual way the number of atoms in the molecule. Na represents both an atom and a molecule of sodium; H_2, O_3, and P_4 are molecules of hydrogen, ozone, and phosphorus respectively.

Allotropy.—Certain elements possess the property of existing in two or more forms which exhibit marked differences both

physical and chemical. This property is called *allot'ropy*, and the more uncommon form is called the *allotropic modification*, or *allotrope*, of the other. Ozone is the allotrope of oxygen; diamond, graphite, and charcoal are allotropic modifications of carbon; and sulfur exists in no less than four forms. These allotropic forms are probably due to difference in number (and possibly arrangement) of the atoms in the elemental molecules.

The Nascent State.—Certain elements, as hydrogen, oxygen, chlorin, and so forth, when just being set free from their compounds, exhibit greater chemical activity than they possess after having stood for a time. This is called the *nascent state*, and such actions are called *nascent actions*. If, for example, hydrogen is passed through water containing silver chlorid in suspension, there is no action; but if the hydrogen be generated in the vessel, the silver chlorid is rapidly decomposed with the production of silver and hydrochloric acid.

The activity of the nascent element is probably due to the fact that the atoms are mainly in the form of free ions, not having had time to gather together into molecules. The nascent state is, therefore, a special form of allot'ropism.

Compound Molecules.—A compound molecule is one which contains two or more kinds of atoms. All such chemical combinations are called *compounds*. These must be carefully distinguished from *mixtures*. In a mixture the different molecules of two or more substances are intermingled, but may be separated by proper means, each substance remaining unchanged. From a mixture of salt and sand the salt may be dissolved out with water, leaving the sand. From a mixture of iron filings and sulfur the iron may be removed with a magnet. In a compound there is but one kind of molecules, and if they are divided the identity of the substance is destroyed. Heat in a test-tube a mixture of iron filings and sulfur. Action takes place, the iron and sulfur unite, and we have the compound iron sulfid, FeS. Iron and sulfur as such have both disappeared and they can no longer be separated by the magnet.

Molecular Compounds.—There is a class of compounds in which two or more molecules are somewhat loosely united, forming what are called *molecular compounds*. Such molecules may often be separated without changing them chemically. In molecular

compounds the parts are separated by commas. An example is common alum, whose formula we write $Al_2(SO_4)_3,K_2SO_4,24H_2O$.

Radicals.—Atoms have a tendency to form groups with one or more points unsatisfied. Such groups are called *Radicals*. They act like single atoms, entering into and leaving compounds without breaking up. They have valence and electric quality like atoms. Hydroxyl, (HO)′, is a univalent negative radical; cyanogen, (CN)′, is a univalent negative radical; methyl, (CH_3)′, is a univalent positive radical; carbonyl, (CO)″, is bivalent and positive. The name of a radical usually ends in yl. In solution and in electrolytic decomposition radicals usually separate as ions.

Ions.—Most substances separate in solution into two or more parts called *ions*, each of which carries a charge of electricity positive or negative. Ions may be *elemental*, corresponding to atoms, or *complex*, corresponding to radicals. When the electric charge is removed they assume the molecular condition. The valence of ions is the same as that of the atoms or radicals which they represent, and the amount of electricity carried by each is 96,530 coulombs per gram-equivalent for each point of valence.

To express ions, as many points or accents are added to the symbol or formula as represent the valence of the ion, the points meaning positive ions and the accents negative ions. Sometimes the plus and minus signs are used. H˙ or $\overset{+}{H}$ is the positive hydrogen ion, SO_4″ or $\overset{++}{SO_4}$ is the negative, bivalent sulfate ion. An ionized molecule may be represented by placing a comma between the ions; as, Na˙,NO_3′.

Naming of Ions.—A very simple method of naming ions is to associate with the word ion the name of the element or radical or some part of the name of the compound. A few examples will illustrate: Na˙, sodium ion or sodion; Fe˙˙, ferrous ion; Fe˙˙˙, ferric ion; Cl′, chlorid ion; HO′, hydroxyl ion; NO_3′, nitrate ion; SO_4″, sulfate ion; SO_3″, sulfite ion. The electric quality may also be indicated in the name; as, Cu˙˙˙, cupric cation; ClO_3′, chlorate anion.

Molecular Weight.—Molecular weight is the weight of the molecule as compared with the weight of an atom of hydrogen. It is equal to the sum of the weights of the atoms in the molecule and also equal to twice the gas density. The term *formula weight* is applied to molecules, ions, or radicals.

Molecular quantity is a quantity of any substance in grams equal to its molecular weight. This is called a *gram-molecular weight* or simply a *mol*. A mol of water is $(1 + 1 + 16 = 18)$ 18 grams.

Volume of a Mol.—A mol of hydrogen is 2 grams, and a liter weighs 0.08995 gram. The volume of a mol of hydrogen is therefore $2 \div 0.08995 = 22.24$ liters. A mol of any other gas under standard conditions occupies the same volume, since gaseous molecules are all of the same size.

Atomic quantity is a quantity in grams equal to the atomic weight. An atomic quantity of oxygen is 16 grams.

Equivalent weight or *gram-equivalent* is a quantity in grams equal to the sum of the atomic weights in a radical or ion, or to the quantity obtained by dividing the molecular weight by the number of hydrogen atoms to which the molecule corresponds; that is, the basicity of an acid, the acidity of a base, the valence of the acid radical in a salt, etc. The following are examples of equivalent weights: $HCl = 36.5$, $SO_4'' = \frac{1}{2}(96) = 48$, $H_3PO_4 = \frac{1}{3}(98) = 32.7$, $Ba(HO)_2 = \frac{1}{2}(171) = 85.5$, $Cl' = 35.5$, $Ca'' = \frac{1}{2}(40) = 20$.

Determination of Molecular Weight.—The analysis of a compound gives simply the proportion in which the constituents enter it. The molecular weight is either the sum of the combining weights or some multiple of this sum. To determine which number represents the molecular weight there are several methods.

1. *By Density.*—Determine the gas density of the substance with reference to hydrogen and multiply the result by 2. The product is the molecular weight. See law of Avogadro.

2. *By Molecular Heat.*—Determine the molecular heat, then take such a multiple of the combining weights as will make the sum of the atomic heats equal the molecular heat. See law of Dulong and Petit.

3. *By Freezing-point of Solutions.*—The depression of the freezing-point has been found to be the same for all equimolecular solutions; that is, solutions which contain quantities of compounds proportional to their molecular weights. See molecular weight by freezing-point.

4. *By Boiling-point of Solutions.*—The elevation of the boiling-point of solutions has a fixed relation to the molecular weight of the dissolved substance. See molecular weight by boiling-point.

In all these methods due allowance must be made for dissociation.

Molecular Formula.—The analysis of water shows that it contains hydrogen and oxygen in the proportion 1 to 8 or 2 to 16. Since the atomic weight of hydrogen is 1 and that of oxygen 16, the relative number of atoms in the molecule will be 2 to 1, and the formula will be H_2O. In hydrogen peroxid the proportion of hydrogen to oxygen is 1 to 16, or by atoms 1 to 1, and the formula is HO. These are called *empirical formulas* and may or may not be the *molecular formulas*. The gas density of water is 9, the molecular weight is therefore 18, which corresponds to the formula H_2O. The density of hydrogen peroxid is 17, its molecular weight 34, and the corresponding formula is H_2O_2. The molecular formulas of water and hydrogen peroxid are therefore H_2O and H_2O_2. In like manner other molecular formulas are determined.

. **Structural Formulas.**—Structural or graphic formulas attempt to show how the atoms are arranged in the molecule. They are obtained by studying (1) molecular formulas, (2) valence, (3) chemical properties and reactions, (4) the formation and decomposition of compounds, beginning with the simpler molecules which can have but one structure and passing step by step to the more complex forms. The following are examples:

$$H-Cl \quad H-O-H \quad H-O-K \quad Ca{=}O \quad Na-O-N{\big<}{}^O_O.$$
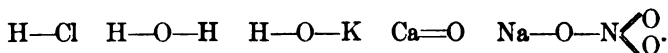
The lines connecting the symbols represent points of valence.

When two structures are possible, that is chosen which best accords with the properties of the compound. The formula of slaked lime may be written H—O—Ca—O—H or H—Ca—O—O—H. That the first is correct is shown by the analogy of the compound to potassium hydroxid, which can only be written K—O—H, the radical OH being characteristic of bases.

When a formula can have more than one structure, it sometimes represents two or more compounds. Such substances are said to be *isomeric*. Isomerism is not common among inorganic substances, but there are numerous organic compounds which present two or more isomers. Examples are:

Ethyl alcohol, H—C—C—O—H;   Methyl ether, H—C—O—C—H
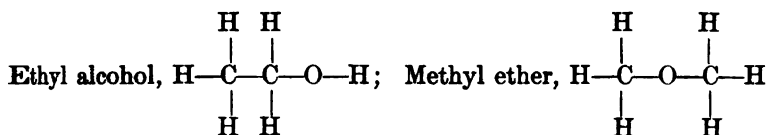
Stereochemistry.—The structural formula written in a plane shows only how the atoms are connected in accordance with valence, and not their actual relative positions in space. We write

marsh-gas H—C—H, while in reality it is probable that the four
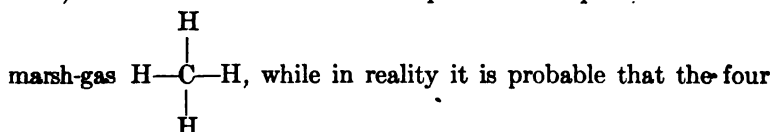
hydrogen atoms stand at the four angles of a regular tetrahedron, the carbon atom being at its center. The study of the spacial arrangement of the atoms in the molecule is called Stereochemistry (Greek *stereos*, solid). The subject is rather difficult because it involves complicated geometric figures.

Classification of Compounds.—Most inorganic compounds may be arranged in two classes, *Binaries* and *Ternaries*.

A binary compound is one in which two kinds of atoms or radicals are directly united, as Na—Cl, Fe=O, (NH₄)—Cl. In each case the one part is positive and the other negative, and no two like atoms are united.

A ternary compound is one in which two kinds of atoms or radicals are united or linked together by means of a third element, as K—O—H, Cl—O—H, K—O—N. Here O is the linking element.

In a sense all compounds may be regarded as binaries formed by the union of two atoms or radicals, the one positive and the other negative. In electrolysis these two parts constitute the ions.

Binary Compounds.—In general each one of the positive elements may unite to each one of the negative elements to form binary compounds. Thus we have compounds of lithium, sodium, potassium, magnesium, and calcium with chlorin, bromin, iodin, sulfur, and so forth. The negative elements also combine readily with one another. We have compounds of nitrogen, phosphorus, arsenic, and sulfur with oxygen, chlorin, bromin, iodin, and so forth. Two positive elements do not readily unite.

Naming of Binaries.—The names of chemical compounds are

derived from their constituent atoms or radicals. The rule for naming binaries is as follows:

Read the name of the positive atom or radical and then the name of the negative with its termination changed to id. Examples: $NaCl$, sodium chlorid; $CaBr_2$, calcium bromid; BaO, barium oxid; Ca_3P_2, calcium phosphid.

In binary compounds the negative element has its normal valence which remains unchanged, but the positive may act with its several valences. Thus there are two oxids of sulfur, SO_2 and SO_3, two chlorids of phosphorus, PCl_3 and PCl_5, several oxids of iron, and so forth. In this case the name of the positive is modified to indicate the valence. The termination is changed for the lower valence to *ous* and for the higher to *ic*. Examples:

SO_2 Sulfurous oxid	PCl_3 Phosphorous chlorid
SO_3 Sulfuric oxid	PCl_5 Phosphoric chlorid

Certain elements act with more than two valences. In this case the prefix *hypo* with the termination *ous* is used for the lowest valence and the prefix *per* with the termination *ic* for the highest. Examples:

FeS Ferrous sulfid	Cl_2O Hypochlorous oxid
FeS_2 Ferric sulfid	Cl_2O_3 Chlorous oxid
FeS_3 Perferric sulfid	Cl_2O_5 Chloric oxid
	Cl_2O_7 Perchloric oxid

In some cases there are more than four compounds and in others there are certain irregularities of valence. The name is made definite, then, by using Greek prefixes to indicate the number of atoms. Examples:

CO_2 Carbon dioxid	Fe_2O_3 Diferric trioxid
N_2O_4 Nitrogen tetroxid	PBr_5 Phosphorus pentabromid

Writing Binary Formulas.—In writing the formulas of binary compounds the number of atoms must be so taken as to make each element furnish the same number of points of valence. In general this number is equal to the least common multiple of the valences. The symbol of the positive is written first.

Three cases arise:

1. The valences are the same and the atoms unite one to one. Examples are taken from compounds of the elements of Groups I

and VII, II and VI, III and V, and of elements belonging to the same group. See Periodic Table.

Valence I. H'F'   Li'Cl'   Na'Cl'   K'Br'   K'I'   Ag'I'   Au'Cl'
Valence II. Gl''O''   Mg''O''   Ca''S''   Ba''Se''   Cd''O''   Sr''S''   Hg''O''
Valence III. B'''N'''   As'''P'''

2. One valence is a simple multiple of the other:

Li$_2$'O'' Ag$_2$'S'' Hg''I$_2$' Na$_2$'S'' Mg''Cl$_2$' C^{IV}O$_2$'' S^{VI}O$_3$'' P^{V}Cl$_5$' Os^{VIII}O$_4$''
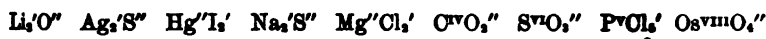
3. The valences are incommensurate:

Ca$_3$''P$_2$''' B$_2$'''O$_3$'' P$_2$^{V}O$_5$'' Gl$_2$^{VII}O$_7$'' As$_2$'''S$_3$'' Al$_2$'''O$_3$'' Ga$_2$'''O$_3$''

Let the student name all the above formulas.

Structure of Binary Compounds.—A few examples will enable the student to understand the structure of these formulas. They must be so written that no two like atoms are united and that all the points are saturated.

Under case 1 above : H—F   Li—Cl   Mg=O   Ca=S   B≡N

Under case 2 : K—O—K   Na—S—Na   O=C=O   O=S=O   O=S⟨O
                                                          O

Under Case 3 : Ca=P—Ca—P=Ca   O=B—O—B=O   S=As—S—As=S

O⟩P—O—P⟨O.
O⟋   ⟍O
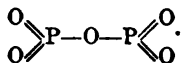
Radicals in Binaries.—Radicals occurring in binary compounds act like elements and are so treated in naming and writing formulas. A few examples will suffice:

(NH$_4$)'Cl' Ammonium chlorid   (CrO$_2$)''Cl$_2$' Chromyl chlorid
Cl'(NH$_2$)' Chloramid   (CH$_3$)'I   Methyl iodid

Pseudo-valence and Free Radicals.—There are certain compounds in which the valence is not really what it appears to be. Hydrogen peroxid, H$_2$O$_2$, is an example. In this formula, which may be written HO, oxygen seems to be a monad. There are good reasons, however, for believing that the oxygen is bivalent and that the formula should be written H—O—O—H. That is, it is formed by the union of two hydroxyl radicals, (HO)'. Oxygen here is said to be a *pseudo-monad*, and hydrogen peroxid is free hydroxyl.

There are many similar compounds, and they are usually

regarded as free radicals and so written as to preserve the theoretical valence. In most cases the vapor density justifies the double formula. When this is not the case, it is supposed that dissociation has taken place and that the radicals remain separate with free points of valence. A good example is found in the oxids of nitrogen, of which there are five, N_2O, NO or N_2O_2, N_2O_3, NO_2 or N_2O_4, N_2O_5, indicating valences one, two, three, four, and five, and violating the rule that valence varies by twos. If the second and fourth formulas be written $O=N—N=O$ and $\begin{smallmatrix}O\\ \diagdown \\ O\diagup\end{smallmatrix}N—N\begin{smallmatrix}\diagup O\\ \\ \diagdown O\end{smallmatrix}$, nitrogen has the valences three and five respectively, thus according with the theory. For practical purposes it is immaterial which way the formula is written, and it is not unlikely that the law of variation of valence by twos may have exceptions.

While it may be said that we write formulas according to valence, it must be remembered that the valence comes from the formula. We give oxygen the valence two because it unites to two atoms of hydrogen, H_2O. We say that the valence of sulfur is four because it unites to two atoms of oxygen, each of which has two points of valence, $S^{IV}O_2''$.

Acids, Bases, and Salts.—Most inorganic compounds can be arranged in accordance with their chemical properties in three classes, *acids*, *bases*, and *salts*. These compounds all ionize more or less in solution and the properties depend upon common or similar ions.

An *acid* is a compound which in solution ionizes, yielding the positive hydrogen ion $H\cdot$ and a negative ion simple or complex. If the negative ion is simple the acid is binary; if it is complex the acid is ternary.

Examples.—Hydrochloric acid, $HCl = H\cdot + Cl'$, binary; nitric acid, $HNO_3 = H\cdot + NO_3'$, ternary; sulfuric acid, $H_2SO_4 = H\cdot + H\cdot + SO_4''$, ternary.

The hydrogen ion is characteristic of the acid. Acids turn vegetable blues red, and this is known as the *acid reaction.*

A *base* is a compound which in solution ionizes, yielding a positive ion usually simple and the negative hydroxyl ion, HO'. Bases are all ternary.

Examples.—Potassium hydroxid, $KHO = K \cdot + HO'$; calcium hydroxid, $Ca(HO)_2 = Ca \cdot \cdot + HO' + HO'$.

The hydroxyl ion is characteristic of the base. Bases turn vegetable reds blue, or restore the blue color when it has been changed to red by acids. This is called the *alkaline reaction.*

A *salt* is a compound which ionizes in solution, yielding a positive ion, usually simple, and a negative ion, simple or complex. If the negative ion is simple the salt is binary if it is complex the salt is ternary.

Examples.—Sodium chlorid, $NaCl = Na \cdot + Cl'$, binary; potassium nitrate, $KNO_3 = K \cdot + NO_3'$, ternary.

In a salt there is no characteristic ion. The cathion is the ion of a base and the anion is the ion of an acid. The reaction of a normal salt is *neutral*, that is, neither acid nor alkaline.

Binary Acids.—The compounds of hydrogen with very negative elements dissociate in solution, yielding hydrogen ions, and are called binary acids. The typical binary acids are the hydrogen compounds of the halogens, Group VII B, viz.:

HF Hydrofluoric acid	HCl Hydrochloric acid
HBr Hydrobromic acid	HI Hydriodic acid

These are all colorless gases which form acid solutions in water.

In like manner, the hydrogen compounds of the sulfoids, Group VI B, may be regarded as weak acids. They are:

H_2O Hydrogen oxid (water)	H_2S Hydrogen sulfid
H_2Se Hydrogen selenid	H_2Te Hydrogen tellurid

Of these the first is water and the other three are colorless. gases soluble in water, and all possess at least one acid character, that of exchanging hydrogen for a metal.

The hydrogen compounds of the nitroids, Group V B, are

H_3N Ammonia H_3P Phosphine H_3As Arsine H_3Sb Stibine

These are all colorless gases, and the last three are scarcely soluble in water. Ammonia is the most soluble of all gases, and its solution in water is strongly alkaline. It has been recently

shown, however, by Frenzel that liquid ammonia is a weak tribasic acid.

In the hydrogen compounds of Group IV the acid character does not appear unless it be evidenced by such compounds as zinc methyl, $Zn(CH_3)_2$.

Binary Salts.—Positive elements and radicals replace the hydrogen of the binary acids to form binary salts. They agree in general properties with the ternary salts. The typical ones are the fluorids, chlorids, bromids, and iodids. In dissociating they yield elemental anions.

Ternary Compounds.—There are three groups of elements which perform the linking function in ternary compounds, viz.:

1. The dyads oxygen, sulfur, selenium, and tellurium. Oxygen forms the typical acids, bases, and salts; sulfur forms the thiocompounds, and the prefixes selen and tellur are used with the compounds of selenium and tellurium.

2. The halogens fluorin, chlorin, bromin, and iodin, two atoms or a double atom acting with a valence II to link the other atoms together. These are called haloacids and halosalts.

3. The triads nitrogen, phosphorus, and arsenic. These compounds are known as ammonia, phosphin, and arsin derivatives, and are not frequently met with in inorganic chemistry.

Of all these compounds those containing oxygen are the most numerous and most important. They fall into three classes, oxyacids, oxybases, and oxysalts, or simply acids, bases, and salts.

Acids.—When the word acid is used it means a binary acid or an oxyacid. The binary acids have already been considered.

An oxyacid is one in which hydrogen is linked by oxygen to a negative element or radical; as, hypochlorous acid, H—O—Cl; nitric acid, $H—O—NO_2$. It dissociates into the hydrogen ion and a complex oxygenated negative ion; as, $HNO_3 = H^{\cdot} + NO_3'$.

Naming of Acids.—Acids are named from the characteristic negative element or radical. To this is given the terminations *ous* and *ic* with the prefixes *hypo* and *per* to indicate valence as in the naming of binaries. Examples:

$HCl'O$	Hypochlorous acid	$HN'''O_2$	Nitrous acid
$HCl'''O_2$	Chlorous acid	HN^VO_3	Nitric acid
HCl^VO_3	Chloric acid	$H_2S^{IV}O_3$	Sulfurous acid
$HCl^{VII}O_4$	Perchloric acid	$H_2S^{VI}O_4$	Sulfuric acid

Ortho and Meta Acids.—In an acid there may be more oxygen than hydrogen, that is, besides the *linking oxygen* which is associated with the hydrogen there may be one or more atoms of *saturating oxygen* united by both points to the negative atom.

An *ortho acid* is one in which all the oxygen is linking and the atoms of oxygen and hydrogen are equal in number.   Examples:

HCl'O   Hypochlorous acid (ortho) $H_3B'''O_3$ Orthoboric acid
$H_4Si^{iv}O_4$ Orthosilicic acid $H_6S^{vi}O_6$ Orthosulfuric acid
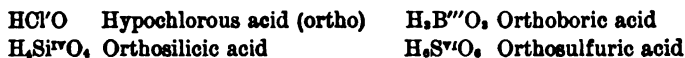
A *meta acid* is one in which there is saturating as well as linking oxygen. If there is one atom of saturating oxygen, it is called *monometa;* if two, *dimeta;* if three, *trimeta.*   Examples:

HN'''O_2 Monometa nitrous acid   HN$^{v}O_3$ Dimeta nitric acid
$H_3P^{v}O_4$ Monometa phosphoric acid $H_2S^{vi}O_4$ Dimeta sulfuric acid
$H_4S^{vi}O_5$ Monometa sulfuric acid   HCl$^{vii}O_4$ Trimeta perchloric acid
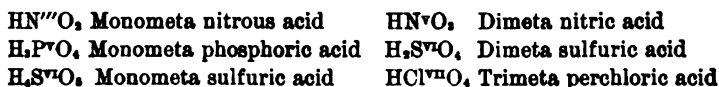
The meta acids may be derived from the ortho by subtracting successive molecules of water, H_2O, thus:

Ortho sulfuric acid, H_6SO_6, less one molecule H_2O gives
Monometa sulfuric acid, H_4SO_5, less another molecule of H_2O gives
Dimeta sulfuric acid, H_2SO_4, less another molecule of water gives
Sulfuric oxid, SO_3, with no hydrogen.

By adding water to SO_3 the acids are formed in the reverse order.

Structure of Acid Molecules.—The structural formulas of acids are easily written by the following rule: Connect each hydrogen atom by an oxygen atom to the negative, then 'connect the remaining oxygen atoms, which are saturating, to the negative by both points.   Examples:

Boric acid B_2BO_3 H—O\
                            H—O/ B—O—H

Nitric acid HNO_3 H—O—N<$\!\!\begin{matrix}O\\O\end{matrix}$

Sulfuric acid H_2SO_4 H—O\ /O
                           H—O/ S \O

Phosphoric acid H_3PO_4 H—O\
                            H—O/ P—O—H.
                                |
                                O
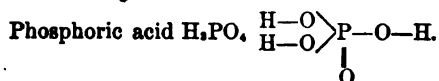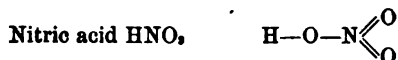
Writing Acid Formulas.—In writing acid formulas note the following facts:

1. The symbols are written in the order of their quality, H first, O last, and the negative between.

2. The termination and prefix of the name indicate the valence of the negative.

3. In ortho acids the number of O's and H's is the same and equal to the valence of the negative. No saturating oxygen.

4. Monometa acids have one O and 2H less than the valence of the negative, one less H than O and one saturating O.

5. Dimeta acids have 2O and 4H less than the valence of the negative, two less H than O and two saturating O's.

6. Trimeta acids have 3O and 6H less than the valence of the negative, three less H than O and three saturating O's.

Example : Write dimeta perchloric acid. Perchloric means highest valence, VII. Dimeta means 2O and 4H less than the valence. Hence the formula $H_3Cl^{VII}O_5$.

The tendency of acids is to contain the smallest amount of hydrogen possible, that is, to assume the lowest meta form. When the name is given without prefix this form is implied. When the valence of the negative is odd there will be one H, and when even 2H. This is illustrated in the common acids:

Valence odd.			Valence even.		
Nitrous acid	$HN'''O_2$	monometa	Sulfurous acid	$H_2S^{IV}O_3$	monometa
Nitric acid	HN^VO_3	dimeta	Sulfuric acid	$H_2S^{VI}O_4$	dimeta
Chlorous acid	$HCl'''O_2$	monometa	Carbonic acid	$H_2C^{IV}O_3$	monometa
Chloric acid	HCl^VO_3	dimeta	Selenous acid	$H_2Se^{IV}O_3$	monometa
Perchloric acid	$HCl^{VII}O_4$	trimeta	Telluric acid	$H_2Te^{VI}O_4$	dimeta

Apparent exceptions to this rule are found in boric acid, $H_3B'''O_3$ (ortho), silicic acid, $H_4Si^{IV}O_4$ (ortho), phosphoric acid, $H_3P^VO_4$ (monometa), and some others.

Basicity of Acids.—The basicity of an acid is measured by the number of hydrogen atoms it contains. It is *monobasic, dibasic, tribasic, tetrabasic,* and so on as it contains one, two, three, four, ·or more atoms of hydrogen. This hydrogen is called *basic hydrogen* because it is readily replaced by positive or basic atoms. The term *polybasic* is applied to acids having more than one atom of hydrogen.

Properties of Acids.—Acids in general possess the following characters:

1. They turn vegetable blues to red.

2. They change the color of many organic substances.

3. They have a sour taste.

4. They corrode and dissolve metals and other substances and destroy organic matters.

5. They readily give up hydrogen for positive atoms or radicals.

6. They neutralize bases, forming salts and water.

7. They ionize in solution, yielding the hydrogen ion.

Illustrations.—Take some dilute hydrochloric acid. Place a drop on blue litmus paper. Add a few drops to a solution of methyl orange and note the change of color. Taste it. Introduce a piece of zinc; it dissolves with the escape of bubbles of hydrogen. To a cubic centimeter of sodium hydroxid solution containing a strip of blue litmus paper add the acid until the color of the paper just changes to red. The acid and base are both neutralized and we have a solution of sodium chlorid (common salt) in water.

Bases.—We have seen that bases yield in solution the hydroxyl ion. A base may be further defined as a *compound in which a positive element or radical is united by oxygen to hydrogen,* or better, *united to hydroxyl.* Examples:

$$K'HO \quad Ca''(HO)_2' \quad Al''(HO)_3' \quad (NH_4)'(HO)' \quad Tl'''O(HO)'.$$
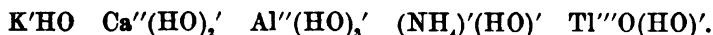
The structure of bases is exactly similar to that of the acids. The above formulas are written thus:

$$K—O—H \qquad H—O—Ca—O—H \qquad \begin{matrix} H—O \\ H—O \end{matrix} \Big> Al—O—H$$

$$(H_4N)—O—H \qquad O=Tl—O—H.$$
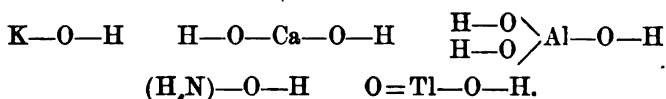
Ortho and Meta Bases.—As applied to bases, the terms ortho and meta mean exactly the same as when applied to acids. The last formula above is a monometa base, having one saturating O. Most bases are ortho.

Naming of Bases.—A base is named by calling the positive element or radical first and adding the term *hydroxid.* The names of the formulas above are potassium hydroxid, calcium hydroxid, aluminum hydroxid, ammonium hydroxid, and thallium metahydroxid. If the positive acts with more than one valence, the

one used is indicated by the syllables *ous* and *ic, hypo* and *per,* as in naming binary compounds. Examples:

$Fe''(HO)_2$ Ferrous hydroxid $Fe'''(HO)_3$ Ferric hydroxid
$Fe^{VI}(HO)_6$ Perferric hydroxid

Writing Formulas of Bases.—Write the symbol of the positive first, then as many hydroxyls as equal the valence of the positive. For meta bases follow the rules given for meta acids.

Acidity of Bases.—The acidity of a base is measured by the number of its hydrogen atoms. It is called *monacid, diacid, triacid,* and so forth, as it contains one two, three, or more atoms of hydrogen. Any base containing more than one atom of hydrogen is called a *polyacid* base. Of the three hydroxids of iron given above the first is diacid, the second triacid, and the third hexacid.

Properties of Bases.—Bases in general possess the following properties:

1. They restore colors which have been changed by acids.

2. They have an alkaline taste. (Taste of potash, soda, or ammonia.)

3. They are caustic, disorganizing animal and vegetable tissues.

4. They do not corrode metals, but dissolve many substances not acted on by acids, such as glass and other silicates.

5. They give up hydrogen for negative atoms or radicals.

6. They neutralize acids, forming salts and water.

7. They ionize in solution, yielding the hydroxyl ion.

Illustrations.—Take some sodium hydroxid solution. Taste it. Place a drop on red litmus paper. Add a few drops to a solution of methyl orange whose color has been changed by an acid. To a cc. of dilute hydrochloric acid containing a strip of litmus paper add the solution until the paper just changes color: the acid and base are both neutralized and we have a solution of sodium chlorid in water.

Salts.—*A salt contains one or more positive elements or radicals united by oxygen to one or more negative elements or radicals.* The simplest case is where both positive and negative are monads, as K'—O''—Cl' potassium hypochlorite.

Salts may be derived from acids by replacing the hydrogen by positives, or from bases by replacing the hydrogen by negatives. They are commonly understood to come from acids.

Naming of Salts.—The name of a salt consists of the name of the positive followed by the name of the negative and both modified so as to indicate their valence. The modifications of the positive are the same as in binaries. The termination of the negative is changed to *ite* for the lower valence and *ate* for the higher; and if there are more than two valences, the prefixes *hypo* and *per* are used. Note that

Hypo—ite	salts come from hypo—ous acids
Ite	salts come from ous acids
Ate	salts come from ic acids
Per—ate	salts come from per—ic acids

Examples:

KCl'O	Potassium hypochlorite	Ca"S^{IV}O$_3$	Calcium sulfite
KCl'''O$_2$	Potassium chlorite	Ba"S^{VI}O$_4$	Barium sulfate
KCl^{V}O$_3$	Potassium chlorate	NaN'''O$_2$	Sodium nitrite
KCl^{VII}O$_4$	Potassium perchlorate	(NH$_4$)N^{V}O$_3$	Ammonium nitrate

Salts are ortho and meta just as the acids from which they are derived, but it is seldom necessary to express this character in the name.

Writing Formulas of Salts.—In writing the formulas of salts it is best to regard them as binary compounds of the positive element with the acid radical obtained by dropping the hydrogen of the acid. The basicity of the acid determines the valence of the radical. Suppose we wish to write the formulas of sodium nitrate, barium chlorate, potassium sulfite, calcium phosphate, and magnesium hypobromite. The acids from which these salts are derived are nitric, chloric, sulfurous, monometaphosphoric, and hypobromic. We may proceed then as follows:

Metal.	Acid.	Radical.	Salt.
Na'	HN^{V}O$_3$	(NO$_3$)'	NaNO$_3$
Ba"	HCl^{V}O$_3$	(ClO$_3$)'	Ba(ClO$_3$)$_2$
K'	H$_2$S^{IV}O$_3$	(SO$_3$)"	K$_2$SO$_3$
Ca"	H$_3$P^{V}O$_4$	(PO$_4$)'''	Ca$_3$(PO$_4$)$_2$
Mg"	HBr'O	(BrO)'	Mg(BrO)$_2$

The order of the symbols is positive first, negative second, and oxygen last.

Structural Formulas of Salts.—In writing the structural formulas of salts attention must be given to four things:

1. The valence of the acid radical.

2. The number of linking O's in each radical.

3. The number of saturating O's in each radical.

4. The valence of the positive element.

Remember also that oxygen must always stand between the positive and the negative.

The valence of the radical is the combined valence of the O's less the valence of the negative.

The number of linking O's is the same as the valence of the radical.

The number of saturating O's is the number of O's less the valence of the radical.

Thus in the radical $S^{VI}O_4$, four O's give 8 points, S has 6; the difference is 2, the valence of the radical and the number of linking O's. Subtracting this from 4, the number of O's, we have 2, the number of saturating O's. The formula is then $\begin{smallmatrix} -O \\ -O \end{smallmatrix}>S<\begin{smallmatrix} O \\ O \end{smallmatrix}$.

The graphic formulas of the five salts last given above are as follows:

$$Na-O-N<^O_O \qquad \begin{smallmatrix} K-O \\ K-O \end{smallmatrix}>S=O \qquad Mg<^{O-Br}_{O-Br}$$

$$\begin{smallmatrix} O \\ O \end{smallmatrix}>Cl-O-Ba-O-Cl<^O_O \qquad Ca<^O_O>P-O-Ca-O-P<^O_O>Ca.$$
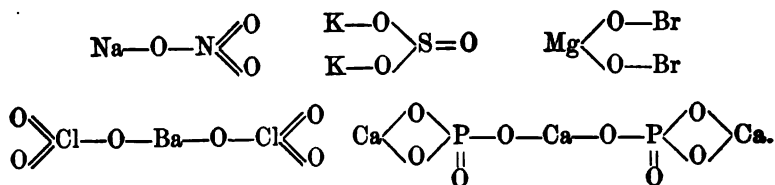
Normal, Acid, Double, and Basic Salts.—A normal salt is one which contains no hydrogen, $NaNO_3$ sodium nitrate; $CaCO_3$ calcium carbonate.

An acid salt is one which contains hydrogen. Only a part of the hydrogen of the acid has been replaced. Acid salts are named by combining the word hydrogen with the name of the salt. $NaHSO_4$ is sodium hydrogen sulfate.

A double salt is one which contains two or more kinds of positive atoms. Part of the hydrogen has been replaced by one element and part by another. The name includes both positive atoms. Double salts may at the same time be acid salts. Examples: $KNaSO_4$ potassium sodium sulfate; $KNaLiPO_4$ potassium sodium lithium phosphate; $KNaHPO_4$ potassium sodium hydrogen phosphate; $CaMg(CO_3)_2$ calcium magnesium carbonate. The graphic

formulas of the first and last will illustrate the structure of these
salts.

$$\begin{matrix} K-O \\ Na-O \end{matrix} \Big\rangle S \Big\langle \begin{matrix} O \\ O \end{matrix} \qquad O=C\Big\langle \begin{matrix} O-Mg-O \\ O-Ca-O \end{matrix} \Big\rangle C=O.$$
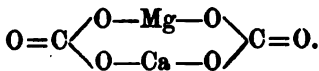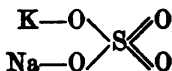
A basic salt is a more or less definite molecular compound of
a normal salt and a metallic oxid or hydroxid. Basic lead car-
bonate is an example, $PbCO_2,Pb(HO)_2$, or $H_2Pb_2CO_5$, or

$$\begin{matrix} H-O-Pb-O \\ H-O-Pb-O \end{matrix} \Big\rangle C=O.$$

Acid salts should have acid properties, basic salts have basic
properties, and normal and double salts are neutral, but there are
many exceptions to this rule.

Properties of Salts.—Salts exhibit the following general
properties:

1. They are neutral—neither acid nor alkaline.
2. They do not change organic colors.
3. They have a salty taste.
4. They are crystalline.
5. They are soluble in water.
6. The color is generally white.
7. They ionize in solution yielding the cation of a base and the
anion of an acid.

To all of this there are many exceptions. Some salts are acid
and some are alkaline, many are insoluble and have no taste,
many are colored and many are amorphous.

Salts are much more numerous than acids and bases. They
include nearly all native inorganic substances. Examples are
found in rocks, clay, soils, and solids generally.

Water Type.—The acids, bases, and salts are formed on what
is called the water type, H—O—H. Replacing an H by a negative
we have an acid; by a positive a base; and replacing one by a
negative and the other by a positive we have a salt. The general
formulas for these classes of compounds are

$$\text{H}-\text{O}-\text{H} \qquad \overset{-}{\text{R}}-\text{O}-\text{H} \qquad \overset{+}{\text{R}}-\text{O}-\text{H} \qquad \overset{+}{\text{R}}-\text{O}-\overset{-}{\text{R}}$$
$$\quad\text{Water} \qquad\quad \text{Acid} \qquad\qquad \text{Base} \qquad\qquad \text{Salt}$$
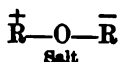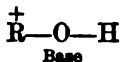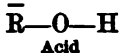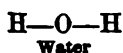
Thio Acids, Bases, and Salts.—Sulfur acts as a linking element and forms compounds similar to the oxygen compounds which we have just considered. These are called *thio* or *sulfo* acids, bases, and salts. Theoretically there should be a sulfur compound for every one of the oxygen compounds, but practically not a great many can be formed. The type is that of hydrogen sulfid, H_2S.

$$\underset{\text{Hydrogen sulfid}}{H-S-H} \qquad \underset{\text{Thio acid}}{\overline{R}-S-H} \qquad \underset{\text{Thio base}}{\overset{+}{R}-S-H} \qquad \underset{\text{Thio salt}}{\overset{+}{R}-S-\overline{R}}$$

The nomenclature is similar to that of the oxygen compounds. A few examples follow:

$H_3As^VS_4$ Thioarsenic acid or sulfarsenic acid
KHS   Potassium hydrosulfid
$AgSb'''S_2$ Silver thioantimonite or sulfantimonite
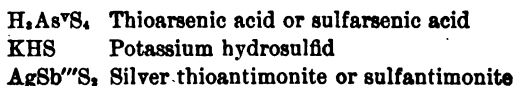
Selenium and tellurium form similar compounds.

Haloacids and Halosalts.—There are many compounds containing fluorin, chlorin, bromin, and iodin which are best explained by supposing that two atoms of the halogen act like one atom of oxygen to perform the linking function. There are two classes of compounds only, *haloacids* when hydrogen is linked by the halogen to a negative element or radical, and *halosalts* when the hydrogen of the haloacid is replaced by a positive atom or radical. These compounds will be understood by the following examples:

$$\text{Fluoboric acid, } HBF_4, \quad H-F=F-B\!\!\left\langle\begin{array}{c} F \\ \| \\ F \end{array}\right.$$

$$\text{Potassium chloroplatinate, } K_2PtCl_6, \quad \begin{array}{c} K-Cl=Cl \\ K-Cl=Cl \end{array}\!\!\bigg\rangle Pt\!\!\left\langle\begin{array}{c} Cl \\ \| \\ Cl \end{array}\right.$$
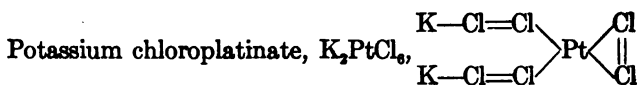
Hydrates.—Water combines to make close chemical compounds with many substances, especially with acidic and basic oxids, the former yielding acids and the latter bases or hydroxids. This may be called *water of constitution*, and when removed involves chemical change.

Water also forms molecular combinations of greater or less complexity, a definite number of molecules uniting with one molecule of the substance. This is called *water of hydration*, and such com-

pounds are called *hydrates.* This water is driven off by heat without involving chemical change. It is usually ignored in writing equations, but must be included in the molecular weight in quantitative work. In expressing it the formula for water is used and separated from the other formula by a comma; for example, $KAl(SO_4)_2,12H_2O$ means that with each molecule of alum there are 12 molecules of water of hydration or crystallization.

Classification of Compounds According to the Negative Element.—A very useful classification of compounds is based upon that part of the name which refers to the negative element. We speak of chlorids, sulfates, sulfites, hypobromites, perchlorates, etc. When these names are used, they commonly refer to the salts of the acids of the negative element, but may include any and all compounds.

The termination id means a binary compound.

The terminations ite and ate mean ternary compounds and imply oxygen.

The following simple definitions will make the matter plain:

· A chlorid is a binary compound of negative chlorin with some other element, generally a metal.

A sulfate is a salt of sulfuric acid.

A sulfite is a salt of sulfurous acid.

A hypochlorite is a salt of hypochlorous acid.

The compounds of the classes thus formed resemble one another more or less closely, particularly when the positive elements belong to the same group.

The principal classes are as follows:

A. Binaries:

    1. Binary acids, HF, HCl, HBr, HI.

    2. Binary salts, Halids—

        a. Haloid salts, NaCl, KBr, RbI, etc.

        b. Other halids—fluorids, chlorids, bromids, iodids, and cyanids.

    3. Oxids of the metals, MgO, FeO, CuO, Na_2O, etc.

    4. Anhydrids—oxids of the non-metals, Cl_2O, SO_2, CO_2, N_2O_3, etc.

    5. Sulfids, selenids, and tellurids, PbS, Fe_2S_3, CuSe, Ag_2Te, etc.

    6. Nitrids, phosphids, arsenids, and antimonids.

7. Carbids and silicids.

B. Ternaries:

1. Hydrates—compounds containing water or hydroxyl.
2. Acids—compounds of negatives with hydroxyl.
3. Bases—compounds of positives with hydroxyl.
4. Salts—positives and negatives united by oxygen.
    a. Of acids of Group VII, chlorates, bromates, hypochlorites, etc.
    b. Of acids of Group VI, sulfates, sulfites, selenates, chromates, etc.
    c. Of acids of Group V, nitrates, nitrites, phosphates, arsenites, etc.
    d. Of acids of Group IV, carbonates, silicates, etc.
    e. Of acids of Group III, borates and aluminates.
5. Thio acids, bases, and salts.
6. Halo acids and salts.

DIVISION II. DYNAMICS.

CHAPTER VIII.

CHEMICAL ACTIONS.

Chemical Affinity.—That force or attraction which holds atoms together in molecules and brings about exchanges of atoms is called *affinity* or *chemism*. While it is convenient to regard it as an attraction, it is proper to remember that there are good reasons for believing that it is but a phenomenon of the energy of the moving atom. It is by the action of this force, energy, attraction, or whatever it may be, that

1. Elemental atoms form elemental molecules, H_2;
2. Dissimilar atoms unite to form compound molecules, HCl;
3. By virtue of superior affinity chemical action takes place, $HCl + NaHO = NaCl + H_2O$. The superior affinity of Na for Cl causes it to exchange places with the H. Although this view of chemical action is modified by the ion theory, it still no doubt closely represents the facts.

Affinity acts at short distances, is strong between atoms that are physically and chemically dissimilar, and weak between those that are similar. Within certain limits it. is irresistible, and in action develops intense energy. There is no physical force which can stop a chemical action where affinity is strong when once it is started.

Molecular Stability.—All molecules are more or less liable to chemical change. They are said to be stable when the change is brought about with difficulty; unstable when the change is easy. Silicic oxid (quartz) and glass are very stable; they resist the action of most chemical agents and are not affected by heat. Carbonates are only moderately stable, being decomposed by heat and acids. Nitrogen iodid and nitroglycerin are very unstable, decomposing with explosive violence upon the slightest provocation.

Molecular stability depends upon the strength of the affinity or attraction between the atoms in the molecule.   Unstable combinations tend always to pass into more stable ones.

Chemical Action and Reaction.—A chemical · *action* is one which results in a chemical change.   It may be a simple decomposition, as when limestone is heated or nitrogen chlorid explodes. Generally, however, two substances are involved and then it is called a *reaction*.   Two or more substances react and one, two, or more are formed.

Chemical Equations.—Reactions are expressed · by chemical equations.   The substances entering the reaction are called the *factors*, and their formulas constitute the first member of the equation; those issuing from the reaction are called the *products*, and their formulas form the second member of the equation.   Since formulas represent molecular weights, the equation tells

1. What substances enter the reaction, and how much of each;

2. What substances emerge from the reaction, and how much of each.

The plus sign means 'acting with' as to the substances, and 'added to' as to weights.   The minus sign is sometimes used.   The sign = indicates equality of weight between factors and products.

There must be no loss.   However the molecules may be changed, every atom in the first member must be found in the second member of the equation.

$$KHO + HNO_3 = KNO_3 + H_2O$$
$$56 + 63 = 101 + 18$$
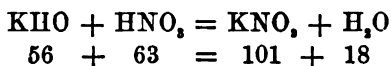
This equation shows that when one molecule of KHO acts on one molecule of HNO_3 there is formed one molecule of KNO_3 and one of H_2O, and that the weights involved are in the proportion of the molecular weights.   Note also that in each member of the equation there is 1K, 2H, 1 N, and 4O.

Writing Equations.—In order to write an equation the products must be known, having been determined by experiment. We can only know that

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
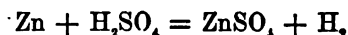
by bringing about the reaction and analyzing the products.   The factors and products being given, the problem is to ascertain how

many molecules of each must be taken in order to preserve strict equality. This can generally be done by simple inspection. Take, for example, the reaction

$$\text{NaCl} + \text{H}_2\text{SO}_4 = \text{HCl} + \text{Na}_2\text{SO}_4.$$
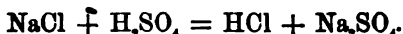
Since 2H is found in the first member, there must be 2H in the second ; and since 2Na is in the second, 2Na must be in the first. We therefore write for the correct equation

$$2\text{NaCl} + \text{H}_2\text{SO}_4 = 2\text{HCl} + \text{Na}_2\text{SO}_4.$$
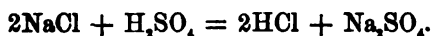
If the equation cannot be completed by inspection, it may be done by a simple algebraic process as follows:

Indicate the number of molecules of each substance by a letter and form a series of simultaneous equations. Assume a value for one letter and solve the equations for the others. Multiply all the values by such a number as will make them all whole numbers and substitute.

If the required equation represents the reaction of copper and nitric acid, we may write it as follows:

$$a\,\text{Cu} + b\,\text{HNO}_3 = c\,\text{Cu(NO}_3)_2 + d\,\text{H}_2\text{O} + e\,\text{NO}.$$

Since the number of atoms of each element must be the same in both members, we have the following equations :

For Cu $a = c$.   For H $b = 2d$.   For N $b = 2c + e$.   For O $3b = 6c + d + e$.

Assuming $a = 1$, we have $c = 1$, $b = 2d$, $b = 2 + e$, and $3b = 6 + d + e$.

Substituting $2d$ for b in the last two equations, we have $2d = 2 + e$ and $5d = 6 + e$. Subtracting, we have $d = \frac{4}{3}$. Continuing the process, we find the following values: $a = 1$, $b = \frac{8}{3}$, $c = 1$, $d = \frac{4}{3}$ $e = \frac{2}{3}$. Multiplying by 3, we have $a = 3$, $b = 8$, $c = 3$, $d = 4$, $e = 2$, and the equation becomes

$$3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu(NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}.$$
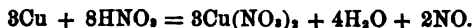
Reactions Molecular.—Since atoms do not as a rule exist free, reactions must take place between molecules. The old molecules must be broken down before the new ones can be formed. This explains why reactions which do not begin spontaneously will go on rapidly when once started. Since equations represent reactions, they should properly be molecular. Practically, however, it is immaterial, and it is usual to write them in their lowest form. The burning of hydrogen may be expressed by $\text{H}_2 + \text{O} = \text{H}_2\text{O}$, or by $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$. The second equation is molecular; the first is not, because one O is only half a molecule.

Volume Equations.—All equations are quantitative, and when the molecular weights are appended the equation is said to be written *by weights* or *gravimetrically*. Equations involving gases may also be written *volumetrically* in accordance with the hypothesis of Avogadro, each molecule representing two volumes, however many atoms it may contain.

In any chemical reaction between gases the volume will remain the same so long as the atomicity of the molecules is unchanged. If the number of atoms in the molecules is increased or diminished, a corresponding inverse change of volume follows. These changes are governed by the valence of the elements. The following reactions illustrate volume equations and volume changes:

1. Monad with monad:
$$H_2 + Cl_2 = 2HCl$$
$$2 \text{ vols.} + 2 \text{ vols.} = 4 \text{ vols.}$$
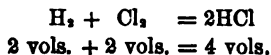
Here 2 volumes of H unite with 2 volumes of Cl to form 4 volumes of HCl; there is no change in volume.

2. Monad with dyad :
$$2H_2 + O_2 = 2H_2O$$
$$4 \text{ vols.} + 2 \text{ vols} = 4 \text{ vols.}$$
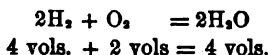
Here 4 volumes of H unite with 2 volumes of O to form 4 volumes of H_2O; there is a reduction in volume from 6 to 4 or from 3 to 2 volumes.

3. Monad with triad:
$$3H_2 + N_2 = 2H_3N$$
$$6 \text{ vols} + 2 \text{ vols.} = 4 \text{ vols.}$$
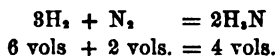
Here 6 volumes and 2 volumes make 4 volumes, a reduction of one half.

4. Monad with tetrad:
$$4H_2 + C_2 = 2CH_4$$
$$8 \text{ vols.} + 2 \text{ vols.} = 4 \text{ vols.}$$
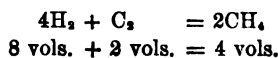
Here 10 volumes become 4 volumes, a reduction of three fifths.

5. Dyad with triad:
$$3O_2 + 2N_2 = 2N_2O_3$$
$$6 \text{ vols.} + 4 \text{ vols.} = 4 \text{ vols.}$$
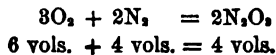
Here again 10 volumes become 4 volumes.

6. Dyad with tetrad :
$$2O_2 + C_2 = 2CO_2$$
$$4 \text{ vols.} + 2 \text{ vols.} = 4 \text{ vols.}$$
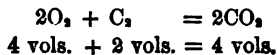
Reduction from 6 to 4, or 3 to 2, volumes.

So any other equation representing gases may be written by volumes.

These equations may be reversed and then represent increase in

volume. If, for example, water be decomposed, every two volumes of steam will give two volumes of hydrogen and one of oxygen, or three volumes of the mixed gases.

Precipitation.—If, on mixing two solutions, an insoluble substance is formed, it is *precipitated,* that is, it appears in solid particles diffused throughout the liquid. The precipitate gathers together and sinks to the bottom or floats on top as its density is greater or less than that of the liquid. If, for example, solutions of potassium iodid and mercuric chlorid are mixed, mercuric iodid precipitates and potassium chlorid remains in solution.

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$
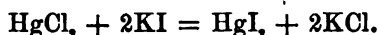
Effervescence.—If, on mixing two solutions, a gaseous substance is formed, it escapes in bubbles, exhibiting the phenomenon called *effervescence.* This is illustrated by placing a piece of zinc in dilute hydrochloric acid, or by adding an acid to a solution of a carbonate:

$$Zn + 2HCl = ZnCl_2 + 2H, \ 2HCl + Na_2CO_3 = 2NaCl + H_2O + CO_2.$$
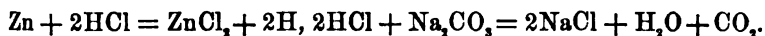
In the first case the escaping gas is hydrogen, and in the second it is carbon dioxid.

Oxidation and Reduction.—By *oxidation* is primarily meant the increase of the relative amount of oxygen in the molecule, while *reduction* means its decrease. Combustion is complete oxidation.

These terms are also extended to mean the increase or decrease of the relative amount of any element which may represent oxygen; that is, a change of valence of elements or ions. We speak of oxidizing ferrous chlorid, $FeCl_2$, to ferric chlorid, $FeCl_3$, or of reducing the chromic ion, $Cr^{...}$ to the chromous ion, $Cr^{..}$.

Catalysis.—Many substances such as water and platinum sponge act by their presence to accelerate chemical actions. Such substances are called *catalysers* or *catalytic agents,* and the action is called *catalysis* or *contact action.* In some cases the action is retarded and then the catalysis is said to be negative. The exact nature of catalytic action is not known.

Cause of Reactions.—Reactions are brought about in various ways, among which are the following:

1. Molecular instability. Many substances are so unstable that it is difficult to keep them. Examples are nitroglycerin, nitrogen chlorid, oxids of nitrogen, and oxids of chlorin.

2. Action of a physical force, viz.:

a. Mechanical action, as in the explosion of a cap;

b. Heat, as in combustion and decomposition by heating;

c. Light, as when CO_2 is decomposed in the leaves of plants;

d. Electricity, as in electrolysis.

3. Superior chemical attraction. This is the usual cause of chemical action, and finds illustration in almost every chemical equation. In the reaction

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
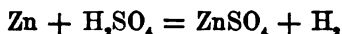
Zn because of its superior attraction for the radical SO_4 is able to displace the H, and the reaction takes place whenever the two substances are brought together.

4. Ionization. Many reactions attributed to superior chemical attraction may also be explained as action of ions. The last equation may be written thus:

$$Zn + H\cdot + H\cdot + SO_4'' = Zn\cdot\cdot + SO_4'' + H_2.$$
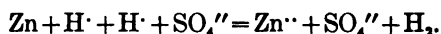
The molecular zinc takes the electric charge from the two hydrogen ions and becomes the zinc ion, while the hydrogen passes to the molecular state.

Conditions Favoring Chemical Change.—Any condition which separates molecules, gives them free motion, or diminishes their stability, or which liberates ions, favors chemical change. Among these conditions are the following:

1. *Fine state of division.* Finely divided lead takes fire spontaneously.

2. *Increase of temperature.* Coal and wood must be heated before they burn.

3. *The nascent state.* Nascent hydrogen is a powerful reducing agent even at the ordinary temperature.

4. *Solution.* Baking-powder keeps so long as it is dry; dissolve, and action takes place at once.

5. *Fusion.* In fusion we have a combination of high temperature and the liquid state, both of which are favorable to chemical action. Iron and copper unite vigorously with molten sulfur.

6. *Vaporization.* The vaporous state is of all the most favorable to chemical action, because the molecules move freely among

themselves. Gases which unite, like oxygen and hydrogen, form explosive mixtures.

7. *Cold.* Many unstable compounds can only be formed at low temperatures. Such are some of the oxids of nitrogen and chlorin, nitroglycerin, phosphonium iodid, and many organic compounds.

8. *The presence of a catalyser.*

9. *Ionization.* Substances in solution are more active when they are ionized.

Rapidity of Chemical Action.—The rapidity of a chemical action will depend upon the stability of the factors, the strength of affinity between the atoms involved, the relative quantities of the substances present (mass action), and the conditions mentioned in the last paragraph.

Classification of Reactions.—Chemical reactions may be arranged in four classes:

1. *Analytic reactions,* in which complex molecules become more simple; as,
$$NH_4NO_3 = N_2O + 2H_2O.$$
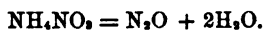
2. *Synthetic reactions,* in which simple molecules become more complex; as,
$$P_2O_5 + H_2O = 2HPO_3.$$

3. *Metathetic reactions,* in which there is a mutual exchange of atoms; as,
$$H_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2HNO_3.$$
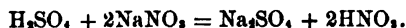
Substitution is a special case of metathesis; as,
$$K + HNO_3 = KNO_3 + H.$$
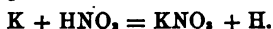
4. *Rearrangement* of atoms in the molecule; as,
$$(NH_4)(CNO) = CO(H_2N)_2$$
Ammonium cyanate.　　Urea.
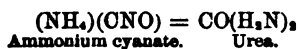
The term *analysis* is often used to indicate the complete separation of the molecule into its elements, while *synthesis* is taken to mean the union of elements to form compound molecules.

Analysis: $CO_2 = C + O_2.$　　Synthesis: $H_2 + O = H_2O.$

Ordinary Chemical Reactions.—Reactions take place usually according to the general law that those substances appear whose formation results in the development of the greatest amount of heat. If free ions are present the reaction will begin spontaneously whenever heat is thereby developed; as,
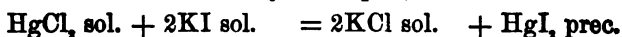
$HgCl_2$ sol. $+ 2KI$ sol. $= 2KCl$ sol. $+ HgI_2$ prec.
49900 cal. $+$ 150000 cal. $=$ 224100 cal. $+$ 24300 cal.
Dif. 24200 cal.

If the heat is not developed, it may be supplied from without and the reaction may still take place; as,

$$H_2SO_4 \quad + 2KNO_3 \quad = K_2SO_4 \quad + 2HNO_3$$
193100 cal. + 239000 cal. = 344600 cal. + 83800 cal.
Dif. — 3700 cal.
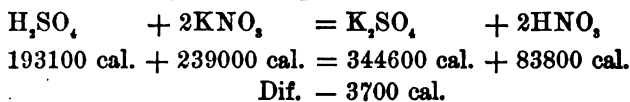
There are several general reactions with which the student should become familiar. If they do not take place spontaneously, they may be brought about by heat or other agents. They are rather arbitrarily arranged as follows:

1. The metals unite to the non-metals.

2. The non-metals unite to one another.

3. The halids, oxids, and hydrogen compounds of the non-metals act upon the metals and their compounds.

4. Acids act upon the metals and their oxids, hydroxids, and carbonates to form salts and water. Unstable acids may at the same time be decomposed.

5. Acids act upon the salts of less stable acids to form the other salt and the other acid.

6. Acids act upon sulfids to form salts and hydrogen sulfid.

7. Bases neutralize acids, but do not as a rule act upon metals.

8. Bases act upon the salts of the unstable acids.

9. Soluble sulfids act upon salts to form sulfids of the metals.

10. All combustibles, metallic and non-metallic, act as reducing agents when heated.

11. Unstable oxids and unstable oxygen compounds act as oxidizing agents in the cold or when heated.

12. The halogens act as indirect oxidizing agents by taking hydrogen from water and setting oxygen free.

13. Metals are separated from many of their compounds by action of reducing agents.

14. Most substances are decomposed or dissociated by heat, many by electricity, and a few by light.

15. Most soluble inorganic substances ionize in aqueous solution.

16. Most reactions which are theoretically possible may be realized by proper use of favoring conditions, as solution, heat, cold, electricity, pressure, etc.

To all of these general reactions there may be exceptions.

Reversible Reactions.—A reaction is said to be reversible when a change of conditions changes its direction. There are many conditions of reversibility, the most important of which are temperature and the relative amounts of the substances involved in the reaction.

If moist ammonium chlorid is heated to 350°, it decomposes into ammonia and hydrogen chlorid. If the temperature is lowered again, ammonium chlorid is re-formed. This fact is expressed in the equation by replacing the sign of equality by double arrows, thus:

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

Hydrogen sulfid precipitates cadmium sulfid from solutions of cadmium chlorid, but the cadmium sulfid dissolves in an excess of the acid,

$$CdCl_2 + H_2S \rightleftharpoons CdS + 2HCl.$$
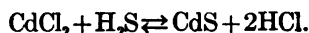
So also, if steam be passed over heated iron, hydrogen is evolved, but if hydrogen be passed over heated iron oxid, water is formed:

$$Fe_3 + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2.$$
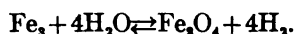
Chemical Equilibrium.—In the second reaction of the last paragraph, if H_2S is in excess, CdS precipitates; if HCl is in excess, CdS dissolves with formation of $CdCl_2$. In any case the reaction will go one way or the other until there is no further change, and then the four compounds all present are said to be in *equilibrium*. Most reactions are reversible and those that are said to be complete are only approximately so.

Law of Mass Action.—The theory of superior affinity as the cause of chemical action was proposed by Torbern Olof Bergmann, a Swedish chemist, in 1775. If the affinity between a and c is greater than that between a and b, the following change will take place:

$$ab + c = ac + b.$$
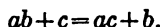
On this principle Bergmann attempted to find the relative affinities of the different elements. Such reactions, however, are generally reversible, and are greatly influenced by the relative amounts of the acting substances. In the years 1864 to 1867, Cato   M.

Guldberg and P. Waage, professors in the University of Christiania in Norway, made investigations which led to the law of mass action which bears their name, and which may be stated as follows:

The amount of chemical change is proportional to the active masses of the substances involved in the reaction.

By *active mass* is meant the number of gram-equivalents in a liter of the solvent. In the reversible reaction

$$a+b \rightleftarrows a'+b'$$
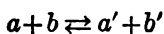
the tendency of a and b to react to form a' and b' will depend primarily upon the nature of the substances, or upon the relative affinities of the atoms which they contain. The action will be modified by physical state, temperature, pressure, degree of ionization, etc. All these may be combined into a factor k, called *coefficient of affinity.* Now the rapidity and the amount of the action will depend upon the number of molecules which meet or collide, and this is measured by the active masses present or by the number of molecules in a given volume. Let p and q represent the active masses of a and b, then the chemical force of the action will be equal to the product kpq. In the same manner, if k', p', and q' be the coefficient of affinity and active masses of b' and c', then the chemical force tending to make a' and b' react to form a and b will be $k'p'q'$. When equilibrium is reached we shall have

$$kpq = k'p'q'.$$

This is the fundamental equation of chemical equilibrium. If the ratio of k to k' be represented by K, then

$$pq = Kp'q'.$$

K is the constant of equilibrium at a given temperature.

Reaction Velocity.—The velocity of the reaction from a and b toward a' and b' is represented by the expression kpq, while the velocity in the opposite direction is $k'p'q'$. The velocity of the reaction as a whole will be equal to the difference between these, viz.:

$$V = v - v' = kpq - k'p'q'.$$

This is the fundamental equation of chemical dynamics.

Complete Reaction.—Since reactions are generally reversible, they will stop when equilibrium is attained in accordance with the law of mass action. If one of the products is removed as fast as it is formed, the influence of its mass is lost, the state of equilib ium will not be reached, and the reaction will go on to completion. This removal may take place in various ways, among which are the following:

1. Evolution of a gas, as in the displacement of hydrogen by metals:

$$Zn + 2HCl = ZnCl_2 + H_2.$$
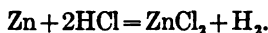
2. Application of heat, one of the substances distilling away, as in preparation of nitric acid:

$$2KNO_3 + H_2SO_4 = K_2SO_4 + 2HNO_3.$$
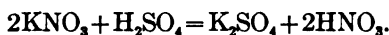
3. Precipitation, as when ions combine to form an insoluble substance:

$$Hg^{\cdot},Cl_2' + 2K^{\cdot},I' = HgI_2 + 2K^{\cdot},Cl'.$$
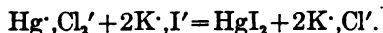
4. Combination of ions without precipitation, as in neutralization:

$$K^{\cdot},HO' + H^{\cdot},NO_3' = K^{\cdot},NO_3' + H_2O.$$
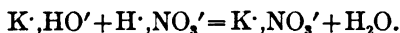
5. Change of ions to atoms, as in electrodeposition:

$$2Ag^{\cdot},NO_3' + H_2O = Ag_2 + 2H^{\cdot},NO_3'.$$
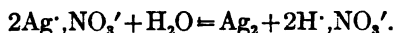
Dissociation.—By the term dissociation is meant a reversible reaction which results in the decomposition of molecules with the formation of (1) other molecules, (2) radicals, or (3) ions. The first case includes reversible reactions generally, and the usual agents are heat (thermolysis) and water (hydrolysis). The second includes those reactions in which molecules are decomposed into atoms or radicals, and here also heat is the usual agent. The third case is ionization, in which the chief agents are water (solution) and electricity (electrolytic dissociation). The phenomena of dissociation are classified according to the agent, and each subject will be treated in its proper connection.

All kinds of dissociation follow the law of mass action.

Thermolysis or Dissociation by Heat.—Many substances when heated separate into their elements or into simpler molecules, and when the temperature is lowered again the parts reunite. This action was first studied by St. Clair Deville in 1857. The density of iodin up to 600° is about 127, showing the molecular formula I_2. Above 1500° the density is only half as large, indicating complete dissociation. If limestone be heated to redness, it breaks up into CaO and CO_2, but when these are cooled together they reunite to form the limestone again: $CaCO_3 \rightleftharpoons CaO + CO_2$. Phosphonium chlorid is not formed at the ordinary temperature by the union of PH_3 and HCl, but at $-20°$ the crystalline solid is produced: $PH_3 + HCl \rightleftharpoons PH_4Cl$.

Dissociation by heat is modified by pressure. If a mixture of PH_3 and HCl be subjected to pressure at 0°, union takes place and under 13 atmospheres it is complete. If the pressure is increased the temperature of dissociation is generally raised and *vice versa*. For each temperature there is therefore a dissociation pressure and for each pressure a dissociation temperature.

Mass Action and Molecular Dissociation.—In dissociation by heat there is a change in the number of molecules, and the conditions of equilibrium will vary with the external pressure. In the reaction $N_2O_4 \rightleftharpoons NO_2 + NO_2$ we have $p = Kp'^2$. In the thermolysis of carbon dioxid, $2CO_2 \rightleftharpoons 2CO + O_2$, we have $p^2 = Kp'^2q'$.

Friedel found that for highly dissociated gases the undissociated portion is proportional to the external pressure.

In the dissociation of a solid, the conditions are somewhat different. The solid acts only through its vapor tension, which is constant for any given temperature and is independent of the active mass. In the reaction $CaCO_3 = CaO + CO_2$ we have $p = Kp'q'$. The only variable here is q', or the pressure of CO_2, and this over a mixture of calcium carbonate and calcium oxid will have a value independent of the masses of these present. This value is called the dissociation pressure of calcium carbonate and it increases as the temperature increases.

The term K is called the *dissociation constant*.

Hydrolysis.—Salts which represent a weak acid or a weak base or both are decomposed more or less completely by water with the formation of the acid and the base. A solution of such a salt will be acid or alkaline as the acid or the base may be the stronger.

For example, a solution of sodium hypochlorite is distinctly alkaline because of the following decomposition:

$$NaClO + H_2O = NaHO + HClO;$$

or in ions:

$$\overset{+}{Na}\cdot + \overset{-}{ClO}' + \overset{+}{H}\cdot + \overset{-}{HO}' = Na\cdot + HO' + HClO.$$
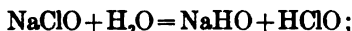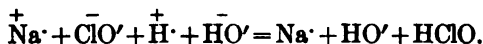
Since hypochlorous acid is weak, there is union between the ClO' ions and the H· ions to form the undissociated HClO, and more water dissociates to supply the hydrogen ions. In this way hydroxyl ions increase in number until the solution is alkaline.

Again, copper chlorid in solution has an acid reaction because of a decomposition which yields free hydrochloric acid:

$$CuCl_2 + 2H_2O = Cu(HO)_2 + 2HCl.$$
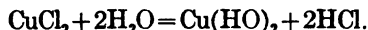
Such decompositions are called *hydrolysis* or *hydrolytic dissociation*.

Neutralization.—When an acid and a base react in molecular proportions, there is formed a salt and water, both of which are neutral. This process is called *neutralization.* If, for example, hydrochloric acid and sodium hydroxid are brought together, sodium chlorid and water are formed:

$$H\cdot,Cl' + Na\cdot,HO' = Na\cdot,Cl' + H_2O.$$
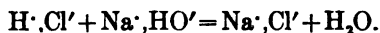
Since the acid, base, and salt are all ionized in the solution, the only chemical action is the union of the hydrogen and hydroxyl ions, $H\cdot + HO' = H_2O$. This reaction, except with very weak acids and bases, is practically complete because water is almost undissociated and hydrogen and hydroxyl ions cannot exist together except in the smallest quantities.

Indicators.—There is no visible change in a mixture when the point of neutralization is reached, but this point may be determined by adding a substance whose color changes when the reaction changes. Such substances are called *indicators.* Those most used are litmus (blue alkaline, red acid), methyl orange (yellow alkaline, red acid), phenolphthalein (red alkaline, colorless acid). Indicators are generally weak acids, but a few are bases. The change in color seems to be due to the formation of salts which differ in color from the indicator.

Several theories have been proposed to explain the action of indicators. That based upon the theory of ions is as follows: If a drop of the indicator is added to an acid solution, its dissociation is reduced practically to zero by the excess of hydrogen ions and the solution will have the color of the undissociated substance. If a base is added the hydrogen ions unite to the hydroxyl ions to form water, and when all are removed the indicator dissociates and the solution takes the color of its anion. If the acid is strong the color change will be abrupt and the point of neutralization will be sharply defined. If the acid is weak the H ions will be so few towards the end of the reaction that the indicator will begin to dissociate and the change of color will be gradual. In this case an indicator must be used whose dissociation is very small (phenolphthalein). If a weak base is to be titrated the indicator should be a relatively strong acid (methyl orange).

Indicators are used to show the end of other reactions. If, for example, silver nitrate is added to a chlorid solution containing potassium chromate, white silver chlorid will be formed until the chlorid ion is all removed, when red silver chromate will begin to form. The first appearance of the red color indicates the end of the reaction. By using solutions of known strength, the strength of other solutions may be determined. This process is much used in analytic chemistry and is called *volumetric analysis*.

Relative Strength of Acids.—Julius Thomsen of Copenhagen and Wilhelm Ostwald of Leipzig investigated the action which two acids have on one base when all are present in equivalent proportions. The base was found to distribute itself between the two acids, the stronger acid taking the larger portion. When one equivalent of sodium hydroxid is mixed with one equivalent each of sulfuric and nitric acids, all in normal solutions, the reaction takes place as follows:

$$H_2SO_4 + H_2N_2O_6 + Na_2H_2O_2 = \tfrac{1}{3}Na_2SO_4 + \tfrac{2}{3}Na_2N_2O_6 + \\ + \tfrac{2}{3}H_2SO_4 + \tfrac{1}{3}H_2N_2O_6 + 2H_2O.$$
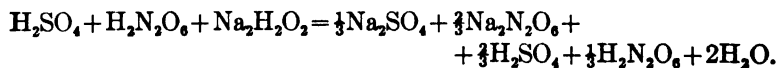
It appears that the amount of sodium nitrate formed is twice that of sodium sulfate, and we may say that nitric acid is twice as strong as sulfuric acid, or that its avidity for the base is twice as great. When hydrochloric and nitric acids are used, the base goes one half to each as follows:

$$2HNO_3 + 2HCl + 2NaHO = NaNO_3 + NaCl + HNO_3 + HCl + 2H_2O.$$
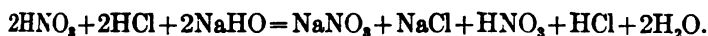
We may therefore say that these two acids have equal strength.

Chemical determination of the composition of the mixture after the reaction was impracticable, and several indirect methods were used, the principal ones being as follows:

1. The thermochemical method of Thomsen, based upon the heats of neutralization of the acids with the base and the heat produced when the acids act upon the salts.

. 2. The volume method of Ostwald, based upon the changes of volume which occur when the solutions of the acids and the base are mixed.

3. The accelerating influence of acids upon certain chemical actions, such as the inversion of sugar.

4. The electric conductivity method of Arrhenius, based upon the theory that the conductivity depends upon the dissociation and that the strength of the acid is measured by the degree of dissociation.

The relative numbers obtained by the different methods do not exactly agree, but the order of strength is practically the same. The numbers for several acids as determined by the thermochemical method, nitric acid being taken as the standard with a strength 100, is as follows:

Nitric acid.	100	Oxalic acid.	24
Hydrochloric acid	100	Phosphoric acid.	13
Hydrobromic acid.	89	Monochloracetic acid.	9
Hydriodic acid.	79	Tartaric acid.	5
Sulfuric acid.	49	Acetic acid.	3

Relative Strength of Bases.—The relative strengths of bases are found by methods very similar to those used for acids. Consistent results were obtained by the study of (1) the distribution of an acid between two bases, (2) the velocity of chemical action of bases, particularly in the saponification of ethereal salts, and (3) the conductivity of different bases. The velocity method gave the following results, lithium hydroxid being taken equal to 100:

Lithium hydroxid.	100	Potassium hydroxid	98
Sodium hydroxid.	98	Ammonium hydroxid.	2

PART III.

PHYSICAL CHEMISTRY.

CHAPTER IX.

STATES OF MATTER.

SOLIDS.

Form and Structure of Solids.—Solids may be homogeneous or heterogeneous. They are homogeneous when they contain only one kind of matter; heterogeneous when they consist of a mixture of two or more kinds of matter. Calcite and quartz are homogeneous; granite and the animal body are heterogeneous.

Solids may be amorphous or crystalline. Amorphous solids are those which have no definite form, such as chalk, limestone, flint. A crystalline solid is one which is composed of crystals. A crystal is a solid bounded by straight lines and plane surfaces so arranged as to make a definite geometric form. Calcite and quartz occur in crystals; marble and granite are crystalline.

Amorphous substances are usually opaque. Crystals are mostly transparent, translucent, or white. Some are colored, but in many cases the color is due to impurities or to water of crystallization.

Crystallization.—When a solution is evaporated the solid separates and usually in crystals. The form and size of the crystals depend upon the nature of the substance and the rapidity of the evaporation. Some solids become crystalline on cooling from fusion; some vapors condense to crystalline solids without passing through the liquid state; and some metals when displaced by chemical action or electrolysis separate in crystals.

Illustrations.—Make a hot saturated solution of common alum and note the fine octahedral crystals which form as it cools. Melt sulfur in a clay

crucible, let cool until a crust is formed on the surface, break the crust
and pour out the liquid, and note the crystals which have formed.   Place
a few crystals of iodin in a flask or tube, heat until the vessel is full of
the purple vapor : crystals form on the cool wall of the vessel.   Place a drop
of mercury in a solution of silver nitrate : the mercury displaces the silver
and the silver is separated in needle-shaped crystals.

Water of Crystallization.—Many substances crystallizing from
solution carry down with them a definite amount of water, called
water of crystallization.   The water is held in the crystals by a
sort of molecular attraction and in molecular proportions, one or
more molecules of water being taken by each molecule of the sub-
stance.   Calcium sulfate (gypsum) takes two molecules of water
to each molecule of the sulfate; copper sulfate, five; iron sulfate,
seven; borax, ten; and alum, twelve.   When such substances are
heated the water is driven off and the crystals fall to powder.   It
is like removing two out of three, five out of six, or twelve out of
thirteen bricks from a wall.

Illustrations.—Heat in a tube a crystal of copper sulfate : the water
expelled condenses on the tube above.   Heat a piece of alum or borax : it
appears to melt, the liberated water of crystallization being so abundant as
to dissolve the substance.   On continuing the heating the water is all driven
off and the dry salt remains.

Many crystalline substances contain no water of crystallization
and are said to be *anhydrous.*   Such are common salt, limestone,
quartz, and potassium chlorate.   These on being heated give off
no water.

Some crystals on exposure to the air gradually lose their water
of crystallization and fall to powder.   This is called *efflorescence.*
Other substances, whether containing water of crystallization or
not, absorb moisture from the air and become damp, or even dis-
solve in the water absorbed.   This is called *deliquescence.*

Illustrations.—Expose a few crystals of iron sulfate to the air for a few
days and note the efflorescence.   Magnesium chlorid and ferric chlorid dis-
solve in moisture absorbed from the air.

Systems of Crystallization.—The axes of a crystal are three or
four imaginary lines passing through its center and terminating
in its faces or angles.   In any given substance the relative lengths
and inclination of the axes and the angles between the correspond-
ing faces are constant.   The general want of geometric regularity

in crystals is due to the fact that some faces are extended and others reduced in size. The position of the faces is determined by the angles which they make with one another or the lengths which they cut off on the axes. The lengths of the axes are computed from the fundamental forms.

Hemihedral forms are those which are obtained by extending alternate faces until they intersect so that one half of the faces are obliterated.

A study of the various forms of crystals shows that they may all be referred to six systems characterized by the length and direction of the axes.

I. ISOMETRIC SYSTEM.—Three axes at right angles to one another and equal.

The fundamental forms are cube, Fig. 8, octahedron, Fig. 9,
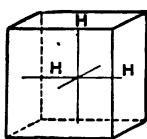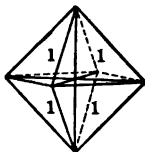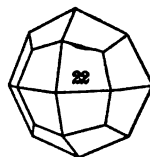
FIG. 8.   FIG. 9.   FIG. 10.   FIG. 11.

rhombic dodecahedron, Fig. 10, and trapezohedron, Fig. 11. These forms occur in various combinations: cube and octahedron, Fig. 12, cube and dodecahedron, Fig. 13, octahedron and dodecahedron, Fig. 14. The tetrahedron, Fig. 15, is a hemihedral form of the octahedron.
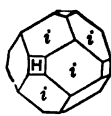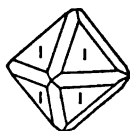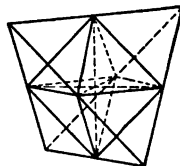
FIG. 12.   FIG. 13.   FIG. 14.   FIG. 15.

Some of the substances cystallizing in this system are common salt, fluor-spar, diamond, garnet, spinel, alum, and iron pyrites.

II. TETRAGONAL OR DIMETRIC SYSTEM.—Three axes at right angles, two equal and one longer or shorter. There are two orders of forms, sometimes distinguished as plus and minus, the axes going in the one to the faces of the prism and in the other to the lateral edges.

The principal forms are the right square prism plus and minus, Figs. 16 and 17, and the square octahedron plus and
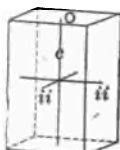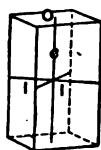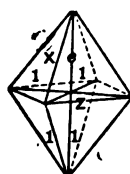
FIG. 16.   FIG. 17.   FIG. 18.   FIG. 19.

minus, Figs. 18 and 19. . The plus and minus tetrahedrons are hemihedral forms of the octahedron, Figs. 20 and 21.

Substances crystallizing in this system are zircon, tin dioxid, yellow prussiate of potash.

III. ORTHORHOMBIC SYSTEM.—Three axes at right angles all of different lengths. The longer axis is called the *macrodiagonal* and the shorter one the *brachydiagonal*. There is often a series of faces variously inclined to the vertical axis. These are called *domes;* those parallel to the longer axis are *macrodomes* and the others *brachydomès.*
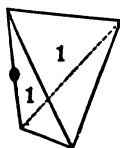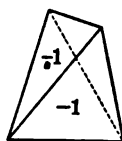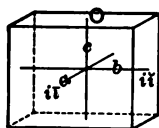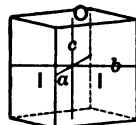
FIG. 20.   FIG. 21.   FIG. 22.   FIG. 23.

The principal forms in this system are the right rectangular prism, Fig. 22, the right rhombic prism, Fig. 23, and the rhombic octahedron, Fig. 24. There are numerous combinations. Fig. 30 represents a crystal of sulfur upon which are seen planes of the rhombic prism, 1, the rectangular prism, *ii*, a series of octahedrons, 1, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$. a brachydome, 1*i*, $\frac{1}{2}i$, and a macrodome, 1*i*.

Substances crystallizing in this system are niter, barium sulfate, aragonite, topaz, and native sulfur.

IV. MONOCLINIC SYSTEM.—Three axes all unequal, two inclined and the third perpendicular to their plane. The principal forms are the oblique rectangular prism, Fig. 25, the oblique

rhombic prism, Fig. 26.   Domes are common as in the ortho-
rhombic system.
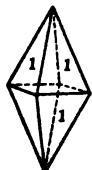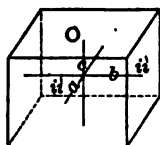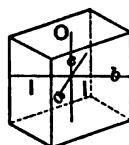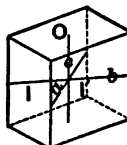
FIG. 24.   FIG. 25.   FIG. 26.   FIG. 27.

    Substances crystallizing in this system are sodium carbonate,
sulfur cooled from fusion, feldspar, selenite, ferrous sulfate, borax,
and cane-sugar.

    V. TRICLINIC SYSTEM.—Three axes all unequal and all in-
clined.   The principal form is the doubly oblique prism, Fig. 27.

    Crystals of this system are seen in copper sulfate, boric acid,
potassium dichromate, and a few other substances.

    VI. HEXAGONAL SYSTEM.—Four axes, three equal and cross-
ing at angles of 60°, the fourth perpendicular to the plane of the
other three and longer or shorter.   The principal forms are the
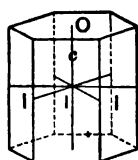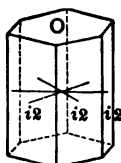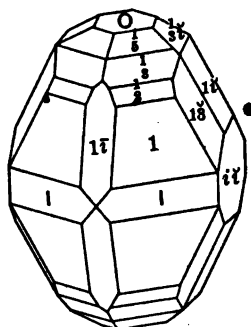
FIG. 28.   FIG. 29.   FIG. 30.

hexagonal prism, Figs. 28 and 29, the hexagonal pyramid, Fig.
31, and the rhombohedron obtuse and acute, Figs. 32 and 33.
The rhombohedron is the hemihedral form of the hexagonal
pyramid, and its relation to the hexagonal prism is shown in Fig.
34.

    Crystals of this system are seen in corundum, quartz, beryl,
calcite, graphite, tourmalin, siderite, apatite.

Iso-, Di-, and Trimorphism.—When two ,or more substances crystallize in the same form they are said to be *isomorphous*. The chlorids, bromids, and iodids of sodium and potassium all crystallize in cubes. The various alums crystallize in octahedrons of the
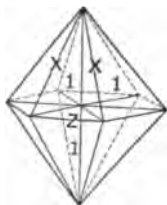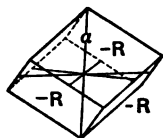
FIG. 31.   FIG. 32.   FIG. 33.   FIG. 34.

isometric system. Calcite, dolomite, and magnesite occur in rhombohedrons of the hexagonal system.

When a substance has two crystalline forms it is said to be *dimorphous*. Sulfur cooled from fusion forms monoclinic prisms; native sulfur occurs in modified rhombic octahedrons. Calcium carbonate is rhombohedral as calcite and orthorhombic as aragonite. Carbon as diamond is isometric; as graphite it is hexagonal.

When a substance crystallizes in three or more systems it is said to be *trimorphous* or *polymorphous*. Sometimes two dimorphous substances are isomorphous in both forms. This is called *isodimorphism*.

<center>LIQUIDS.</center>

Character of a Liquid.—In a liquid the molecular attraction is so weak that the body cannot retain its shape without support. It must therefore be contained in a vessel, and its free surface is everywhere parallel with the surface of the earth. When the wall of the vessel is removed the liquid flows away in that direction which brings it to the lowest level.

Equilibrium.—When all points of the surface of a liquid are at the same level, there is no tendency to flow and it is said to be in equilibrium. If one point is lower than another the liquid flows toward the lower point. Liquids stand at the same level in communicating vessels, but if the liquid in one vessel has a greater density than that in the other, it will stand at a lower level, and the difference of level will vary as the difference of density.

Illustrations.—Partly fill a U tube with water and note the level in the two arms. Add to one arm some alcohol and note again the level. Repeat the experiment with mercury and water.

Fluidity and Viscosity. — The strength of the molecular cohesion in a liquid determines its fluidity. If the attraction is small and the flow easy, the liquid is said to be *limpid;* if the attraction is strong and the flow difficult, the liquid is said to be *viscous.*

Buoyancy.—If a solid is immersed in a liquid, it is buoyed up by a force equal to the weight of the water displaced. If the density of the solid is less than that of the water, it will float; if greater, it will sink and rest upon the bottom with a pressure equal to the difference between its weight and the weight of the water displaced. This is the principle of specific-gravity determinations with the hydrometer and by weighing in air and in water.

Surface Tension.—The free surface of a liquid is composed of a sheet of molecules which are in a state of tension and press with a certain force upon the liquid below. This is called *surface tension.* If the quantity of the liquid is small, as in drops of water, the effect of this pressure is to make it assume the spherical shape. The liquid may have two surfaces of tension, as in the soap-film; or the double film may enclose a gas, as in the soap-bubble; or a gas may be surrounded by the liquid, as with bubbles of air in water; or the films may bound two liquid surfaces, as when drops of oil float in water.

Surface tension is measured in various ways. In the capillary method the height to which the liquid rises in a capillary tube is measured and from this the tension is calculated.

Surface tension affords a means of ascertaining the molecular complexity of liquids. Investigations by this method have shown that most liquids are normal; that is, the liquid molecule has the same composition as the gas molecule. In some cases the molecules are associated or condensed into complex aggregates. The molecule of water is thus shown to have the formula $(H_2O)_4$.

GASES.

Kinetic Theory of Gases.—The peculiar properties of gases are explained by what is called the *kinetic theory of gases.* This theory

supposes that the molecules are continually moving with great rapidity in straight lines, and are so far apart that their mutual attraction is small. The moving molecules are constantly impinging against one another and against the walls of the container and rebounding with perfect elasticity. This impact of the molecules gives rise to the force which is called *pressure.* Since the molecules are very light and but slightly influenced by gravity, the pressure is practically equal in all directions.

Pressure of Gases.—If a gas is unconfined, it tends to expand indefinitely, because the surface molecules meet with no resistance. If the gas is confined, the molecules impinging upon the wall of the container produce a pressure the force of which will depend upon the quantity of gas within the space. If we double the quantity, the pressure is doubled, and if we diminish the quantity, the pressure is correspondingly diminished.

The force with which a gas tends to expand when external pressure is removed is called its *tension.* The tension is equal to the external pressure. The two words may therefore be used interchangeably.

Partial Pressure of Gases.—If two or more gases are contained in a vessel, each expands and fills the space as if the others were not present, and each exerts its own pressure upon the walls of the vessel. This is called *partial pressure.* The sum of the partial pressures is the total pressure.

Atmospheric Pressure.—The atmosphere is a great aerial ocean which surrounds the earth and exerts a pressure upon all bodies. This pressure is greatest at the surface and diminishes rapidly upward. The pressure of a gas is apparently zero when it is equal to that of the atmosphere; it is minus when less than and plus when greater than the atmospheric pressure.

The Barometer.—If we take a tube more than 760 mm. long, closed at one end, and fill it with mercury and invert in a vessel of mercury, the column will fall until its weight just balances the weight of the outside air. By measuring the length of this column of mercury we obtain a measure of the atmospheric pressure. Such an instrument with the scale attached for the measurement is called a *barometer.* The empty space at the top of the tube is called the *Torricellian vacuum,* because it was first discovered by Torricelli, a Florentine, in 1643.

Two kinds of mercury barometer are in use, the cistern barometer and the siphon barometer. In the former the tube dips into a cistern which is provided with an arrangement by which the mercury can always be brought to a fixed level. A brass scale with vernier is attached by which the height of the column can be read very accurately.

The siphon barometer is much used in laboratories and is very convenient. It is a bent barometer-tube with the two limbs graduated in opposite directions so that the difference of the readings is the barometric height.

Readings are always taken at the top of the meniscus and the line of sight should be horizontal to avoid error due to parallax.

Barometer Corrections.—Since mercury expands when heated, the column which balances the atmosphere becomes longer as the temperature rises. The length of the column at 0° is taken as the standard. The coefficient of expansion of mercury for a change of 1° is 0.000182, and the formula for reduction to 0° is

$$h_0 = h(1 - 0.000182t).$$

The scale also is affected by heat. The coefficient of expansion is for glass 0.000155 and for brass 0.00002. Since the scale and the mercury expand in the same direction, the true error will be the difference between the expansions, and the correction for both scale and temperature will be for glass $h_0 = h(1 - 0.000027t)$ and for brass $h_0 = h(1 - 0.000162t)$.

Other slight corrections are made in very accurate work for latitude and for the depression of the column due to capillary action and the vapor tension of mercury.

Standard Pressure.— All gases sustain considerable changes of volume under changes of pressure. When, therefore, a gas is measured, the reading of the barometer must be taken so that the pressure upon the gas may be known, and the volume must be corrected to some standard pressure. The standard usually adopted is the weight of a column of pure mercury at 0° and 760 mm. (29.922 inches) high. This is about the average pressure of the atmosphere at sea-level in latitude 45°. It is equal to 1033.296 grams per square centimeter or 14.69 pounds per square inch.

Elasticity of Gases.—Gases are perfectly elastic. After having been compressed they return to the original volume when the pressure is removed, and they give out as much energy in expanding as was used in compressing them.

The Air-pump.—The air-pump is an instrument for removing air or other gases from closed vessels. The highest vacuum is obtained with the mercury-pump, in which the Torricellian vacuum is made use of, and the Sprengel pump may be taken as an illustration. It consists of a long barometer-tube furnished with a funnel, stop-cock, and side tube, and dipping below in a vessel of mercury. The side tube is attached to the vessel to be exhausted and mercury is allowed to flow slowly down the tube. Gas is drawn in from the side tube and goes down with the mercury, separating the column into sections. When the exhaustion is complete the mercury flows in a continuous column.

With the common metal pump a vacuum representing a pressure of one millimeter of mercury is considered good, but with the mercury-pump the pressure may easily be reduced to one thousandth of a millimeter or one millionth of an atmosphere. Such a pump is used in exhausting the incandescent electric-light bulbs.

Gas Laws.—Gases have been found to act in accordance with three remarkable laws, the discovery of which has profoundly influenced the development of chemical science. They are known as the law of Boyle, the law of Gay-Lussac, and the law of Avogadro. The first relates to the effect of pressure upon gas volume, the second to the effect of temperature upon gas volume, and the third to the volume of the gas molecule. The last has already been explained.

Boyle's Law.—This law was discovered by Robert Boyle of England in 1662, and independently by the Abbé Mariotte in 1679. It may be stated in three phases as follows:

1. The volume of a given weight of a gas varies inversely as the pressure upon it.

2. The weight of a given volume of a gas varies directly as the pressure upon it.

3. The density of any gas varies inversely as the volume and directly as the pressure.

This is expressed algebraically as follows:

$$v : v' :: p' : p, \quad vp = v'p' = \text{a constant, and} \quad v = \frac{v'p'}{p},$$

in which v is the volume of a given weight of gas at a pressure p, and v' the volume of the same gas at the pressure p', the temperature remaining the same. If d and d' represent the densities of volumes v and v' under the pressures p and p', then

$$d : d' :: pv' : p'v, \quad \text{and} \quad d = \frac{d'pv'}{vp'}.$$

The law may be demonstrated as follows:

Take a bent glass tube with unequal arms, having the shorter arm closed. Pour mercury into the tube until the bend is closed and the mercury stands at the same height in both arms. The enclosed air is now subjected to a pressure of one atmosphere. Add more mercury to the tube and note that as the longer arm fills, the volume of air in the shorter arm diminishes. When the difference in level of the mercury in the two arms is 760 mm., that is, when the pressure upon the enclosed air is two atmospheres, it will be found that the volume has been reduced one half.

This law holds for most gases within the ordinary range of temperature. As the temperature is lowered and the pressure increased certain deviations are observed. As the gas approaches the critical temperature and pressure, that is, the point at which it begins to liquefy, this deviation is considerable, and different for different gases.
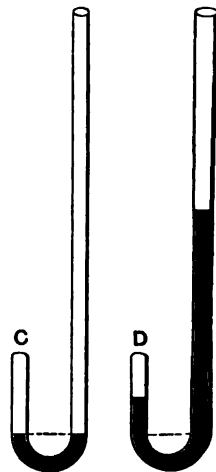
Fɪɢ. 35.

The diagram, after Natterer, illustrates the action of hydrogen and of ethylene at 60°. If the law were strictly followed, the lines would be straight and parallel to the horizontal axis.

Gas Volume and Temperature. Law of Gay-Lussac.—The effect of changes of temperature upon the volume of gases was investigated by Gay-Lussac of Paris in 1802, and later by John Dalton of England and Jacques A. C. Charles of France. It was found that within rather wide ranges of temperature and for most gases an increase of one degree caused an increase of volume equal to about $\frac{1}{273}$ of the volume at 0°. This law, which is called the *law of Gay-Lussac*, or of Dalton, or of Charles, is expressed by the equation

$$v = v_0\left(1 + \frac{t}{273}\right), \quad \text{or} \quad v = v_0(1 + 0.003665t),$$

in which $v=$ the volume at temperature t and $v_0=$ the volume at 0°.
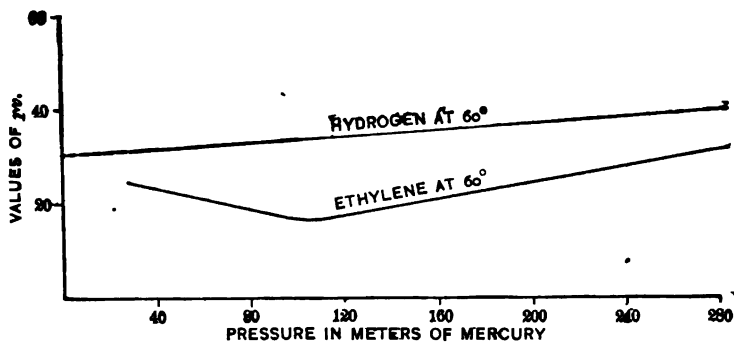
FIG. 36.—DEVIATIONS FROM BOYLE'S LAW.

Changes of volume and of pressure follow the same law, and if we substitute p for v we have

$$p=p_0\left(1+\frac{t}{273}\right), \quad \text{or} \quad p=p_0(1+0.003665t),$$

which is the equation for pressure change due to change of temperature.

If pressure and volume are both allowed to change, the effect will be divided between them and we shall have

$$pv=p_0v_0(1+0.003665t),$$

which equation combines the laws of Boyle and Gay-Lussac. If $p_0=760$ millimeters the equation may take the form

$$pv=v_0\times\frac{760(273+t)}{273}, \quad \text{or} \quad v_0=v\times\frac{p}{760}\times\frac{273}{273+t}.$$

The last expression is much used for reducing gas volumes to standard conditions of pressure and temperature. When gases are measured over water, p will equal the barometer reading minus the aqueous vapor tension for the temperature t.

Deviations from Gas Laws Explained.—The deviations from the laws of Boyle and Gay-Lussac are explained by the kinetic theory

of gases. In these laws the volume occupied by the molecules themselves is not taken into consideration. When the pressure is low, the molecular interspaces are large compared with the size of the molecules. When the pressure is high, the space occupied by the molecules is considerable. In the case of hydrogen the product pv is always higher than it should be. This was explained by Natterer to be due to the fact that the molecules occupied space. If this space is represented by b, the equation becomes $p(v-b) = RT$, T being absolute temperature $(273+t)$, and R representing $\frac{p_0 v_0}{273}$, which is constant when $p = 760$ mm.

With many gases, as the pressure decreases, the value of pv becomes too small. Van der Waals ascribed this deviation to the mutual attraction of the molecules which would act in the direction of the pressure. This attraction is inversely proportional to the square of the distance between the molecules. This distance varies as the square of the density, or inversely as the square of the volume. If a represents the molecular attraction when the gas occupies unit volume, the pressure increment for any volume v is $\frac{a}{v^2}$, and the equation becomes

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT.$$

This is known as *Van der Waals' equation.* Amagat found the constants for ethylene to be $a = 0.00786$ and $b = 0.0024$. With these numbers he obtained the following very satisfactory results, p representing atmospheres and v being equal to 1000 when p equals 1:

p	pv Observed.	pv Calculated.
1.0	1000	1000
45.8	781	782
176.0	643	642
282.2	951	940

The value of the constant R may be computed. A cubic centimeter of mercury weighs 13.29 grams and p_0 represents a pressure of $76 \times 13.59 = 1033$ grams per square centimeter. The volume v_0 of one molecular weight of a gas is 22,240 cubic centimeters. The

value of R then becomes

$$R = \frac{22240 \times 1033}{273} = 84153.$$

Mass Action and Gases.—When a reaction takes place between gases with a gaseous product, the partial pressure of each constituent gas will be proportional to the number of its molecules, or to the active masses, and hence pressures may be substituted for masses in the equation of equilibrium. In the reaction $H_2 + I_2 = HI + HI$, we shall have, according to the law of mass action, since $p' = q'$,

$$pq = Kp'^2,$$

in which p, q, and q' represent the partial pressures of H, I, and HI respectively. In this reaction Lemoine found the value of the constant to be at $440°$ $K = 0.0375$. Since in this case there is no change in the number of molecules, the constant K, or the condition of equilibrium, is independent of the external pressure, because if the pressure is changed, each partial pressure is changed in the same ratio.

CHAPTER X.

CHANGES OF PHYSICAL STATE.

SOLID AND LIQUID.

Fusion and Solidification.—If the temperature of a solid is sufficiently raised, it becomes a liquid and is said to *fuse* or *melt*. If the temperature of a liquid is sufficiently lowered, it becomes a solid and is said to *freeze* or *solidify*. The temperature at which a solid becomes a liquid is called its *melting-* or *fusing-point,* and the temperature at which a liquid becomes a solid is called its *freezing-* or *solidifying-point*. For any one substance the two points are generally one and the same. Some substances change their state abruptly, like ice, while others, like iron, soften and become plastic before melting.

To determine the melting-point, the solid is placed in a small glass tube which is attached to a thermometer, and the whole is immersed in a liquid which boils at a temperature above the melting-point to be determined. The liquid is heated and the temperature noted at which the solid melts. Such determinations have little accuracy.

To determine the freezing-point, the liquid or the melted solid is slowly cooled until it begins to solidify and the temperature noted with an immersed thermometer. In this case precaution must be taken against *undercooling*. Liquids will generally cool below the freezing-point before solidification begins. If a solid fragment of the same substance be added to an undercooled liquid, solidification begins at once and the temperature rises to the true freezing-point. These determinations are quite accurate.

Change of Volume during Fusion.—Bodies expand as the temperature rises, and this expansion usually continues during the process of fusion. There are many exceptions, however, as in the case of crystalline solids. These generally expand on ·solidifying and hence contract when they melt. The change of volume is

106

always small. In the case of water it is unusually large, 100 volumes becoming 109 of ice.

Effect of Pressure on the Melting-point.—Increase of pressure lowers the melting-point of substances which expand on solidifying, and raises the melting-point of those which contract; the change in any case is small.

Heat of Fusion.—When heat is applied to a solid the temperature rises regularly until it begins to melt, then remains constant until the fusion is complete. The heat that passes into the body during fusion is called *latent heat of fusion*, or simply *heat of fusion*. It is heat energy used in loosening and separating the molecules and increasing their motion as the body passes from the solid to the liquid state. A like amount of heat is given out when a body passes from the liquid to the solid state.

Illustration.—The latent heat of ice may be determined by the method of mixtures. One kilogram of crushed ice at 0° and one kilogram of boiling water at 100° are mixed. When the ice is all melted the temperature will be 10°. The temperature of the water was lowered through 90°, but 10° of this was used in warming the melted ice from 0° to 10°, so 80° disappeared. The heat of fusion of ice is therefore 80 heat-units.

Freezing Mixtures.—When a salt is dissolved it virtually passes into the liquid state and heat is absorbed in the process. If a mixture of salt and ice be brought together, the salt compels the liquefaction of the ice in order that it may dissolve in it. In this liquefaction heat must become latent and so the temperature of the mixture is lowered. Two and a half parts of powdered ice and one of salt will give a temperature of $-18°$ C. or 0° F.

SOLID AND GAS.

Kinetic Theory of Solids and Liquids.—According to the kinetic theory the molecules of solids and liquids, as well as those of gases, are in active motion. Those molecules which are near the surface are liable to pass beyond the attractive influence of their fellows and fly away. This escape of molecules is called *evaporation*.

Evaporation of Solids.—Many solids have a measurable vapor pressure and pass directly into the gaseous state. Ice gradually disappears by evaporation, even when the temperature is far

below 0°. The odor of solids like gum camphor is due to escaping vapors.

Sublimation.—Some solids when heated sublime; that is, they become gaseous and on cooling condense to the solid again without passing through the liquid state. Good examples are iodin and arsenous oxid. Sublimation will take place when the solid has at its melting-point a vapor pressure not far from the atmospheric pressure, or when the boiling- and melting-points are close together. Solids sublime under reduced pressure because of the lowering of the boiling-point.

LIQUID AND GAS.

Evaporation of Liquids.—Evaporation takes place from the surface of all liquids. Since it is those molecules which have the highest molecular energy that escape most easily, the mean temperature of the remaining liquid is lowered. Evaporation is therefore a cooling process. If the escaping molecules are continuously removed, as by a current of air or into a vacuum, the evaporation goes on more rapidly.

Illustrations.— Place a drop of ether or chloroform on the back of the hand and note the cooling effect.

Moisten the bulb of a thermometer with water and place it by the side of a thermometer with a dry bulb and note the difference of reading.

Vapor Tension.—If the space over a liquid be occupied by a gas, the escaping molecules collide with the molecules of the gas, giving rise to a certain pressure. If the space is limited, the evaporation continues until such a pressure is reached that as many molecules are returned to the liquid as leave it. This pressure, which remains constant for any given liquid and temperature, is called *vapor pressure* or *vapor tension*. It rises with the temperature until at the boiling-point of the liquid it is equal to the pressure of the atmosphere.

Illustration.—Fill a barometer-tube with mercury, invert over mercury, note the height of the column, and then introduce a few drops of water. The distance through which the mercury falls measures the vapor tension of water. Add a few drops of alcohol: the fall is its vapor tension.

In all nice experiments where gases are collected over water corrections must be made for vapor tension. Even barometric readings must be reduced for the tension of mercury vapor. Special tables are prepared for this purpose.

Ebullition.—As the temperature of a liquid rises evaporation from the surface continues with increasing rapidity until a temperature is reached at which the vapor tension is equal to the pressure of the atmosphere, then bubbles of vapor form throughout the liquid, pass through it and escape. This is *ebullition* or *boiling*. The boiling continues so long as the heat is applied. The temperature ceases to rise when the boiling begins, and remains constant until the liquid is all boiled away. Increasing the heat simply makes the boiling more rapid. If the heat is removed, the boiling stops at once, the evaporation soon cooling the liquid below the boiling temperature.

Boiling-point.—The temperature at which a liquid boils is called its *boiling-point*. This is constant for any substance but varies with the pressure, because pressure hinders the escape of the molecules. Increase of pressure raises the boiling-point and diminution lowers it. Light liquids at the ordinary temperature and water but slightly warmed boil freely in vacuo.

The range of boiling-points is almost as great as the range of measurable temperatures. Liquid hydrogen boils at a point but a few degrees above absolute zero, and carbon is scarcely volatilized at the highest temperature of the electric furnace. Water, which is the common standard of reference, boils at 100° under the standard atmospheric pressure of 760 mm.

When water is heated in a clean glass vessel it rises to a temperature somewhat above 100° before ebullition begins. It is then said to be superheated. If now the temperature be raised a little higher, or if the water be shaken or stirred, or if a solid be dropped into it, or if a bubble of gas be passed through it, large bubbles of steam are suddenly formed, often with explosive violence. This is called *bumping*. It may be largely prevented by placing in the vessel small pieces of glass or spongy platinum.

Since liquids are liable to be superheated, the boiling temperature must be determined by placing the thermometer in the vapor and not in the boiling liquid.

Illustration.—The boiling of a liquid under diminished pressure is simply illustrated as follows : Fill a flask one third full of water and heat to boiling. Close tightly with a rubber cork. Invert the flask and sprinkle cold water upon it. The cold water condenses the steam, reducing the pressure, and the water in the flask boils vigorously.

Heat of Vaporization.—We have seen that after a liquid begins to boil the temperature remains constant. The heat is consumed in overcoming cohesion and separating the molecules to a greater distance from one another. The quantity of heat required to effect this is definite for each substance and is called *heat of vaporization*. It is also called *latent heat* because it disappears as heat, being converted into kinetic molecular energy. The same quantity of heat is restored or given out when the vapor condenses back to the liquid.

The heat of vaporization of water is 536 calories, that is, to convert one gram of water at 100° into one gram of steam at 100° requires enough of heat to raise 536 grams of water through one degree, or to raise 5.36 grams from 0° to 100°.

Trouton's Law.—The molecular heat of vaporization of a liquid, that is, the heat required to produce a mol. of gas at the absolute boiling-point $t°$, was found by Trouton in 1884 to be about $21t$ calories, $2t$ calories of which were expended against atmospheric pressure. This is known as *Trouton's law* and may be stated thus: *The molecular heat of vaporization is proportional to the absolute temperature at which the liquid boils.* Thus, the heat of vaporization of benzene, molecular weight 78 and boiling-point 80°, is 94, and therefore its molecular heat 94×78 divided by its absolute boiling-point $80 + 273 = 20.7$.

This law holds good for most liquids and shows that liquid molecules are identical with gas molecules and not polymers, as has usually been supposed.

Distillation.—If the vessel which contains a boiling liquid be connected with a coiled tube surrounded with cold water, the vapor is cooled and condensed back to liquid form. This process is called *distillation*, the apparatus is called a *still*, the coiled tube is the *worm*, and the cooling vessel is the *condenser*.

Liquefaction of Gases.—The physical state of a substance depends upon its temperature and the pressure upon it. Solids

and liquids are converted into gases by raising the temperature or lowering the pressure or by combining the two processes. So gases are liquefied and solidified by the reverse process of lowering temperature and increasing pressure.

When a substance which is solid or liquid at the ordinary temperature and pressure has been gasified by heat, it returns to the original state on cooling. Substances which are gases under ordinary conditions are only liquefied by bringing about artificial conditions of cold and pressure. The means used are the condensing pump or a column of mercury for obtaining pressure, and the sudden expansion of gases or the evaporation of liquid gases for obtaining cold.

Liquefaction by Pressure.—Some gases are liquefied by pressure alone at the ordinary temperature or with moderate cold. Such are ethylene, carbon dioxid, acetylene, ammonia, chlorin, etc. Other gases cannot be liquefied without a further lowering of the temperature.

Cooling by Sudden Expansion.—If a gas be subjected to great pressure and then be allowed to expand by the removal of the pressure, its temperature is very much lowered, and the gas may become a liquid in the form of a fine mist. This may be shown by a simple experiment. Close a flask which contains a small quantity of water with a cork through which passes a tube. Apply the mouth to the tube and by sudden suction lower the pressure in the flask. A cloud of mist appears. The water vapor has been condensed by the cooling due to the sudden expansion of the air.

The profound cooling effect of great changes of pressure is shown by the following table, which is for air at 0° and shows the temperature obtained by suddenly reducing the pressure to one atmosphere:

Pressure at 0°	100 at.	200 at.	300 at.	400 at.	500 at.
Temperature at 1 at...	− 210°	− 214°	− 221°	−225°	− 228°

Cooling by Evaporation.—If liquid gases are caused to evaporate rapidly, the temperature is greatly lowered. This may be done by exposing them to the atmosphere, or better by connecting the vessel containing them with an exhaust-pump. Liquid carbon dioxid thus evaporating is cooled to − 70°, liquid ethylene to − 120°, and liquid oxygen to − 200°. By using one after the

other of these refrigerating liquids almost any degree of cold **may** be obtained. Indeed temperatures have been reached within 15° or 20° of the absolute zero.

Subjected to these very low temperatures most gases liquefy at the ordinary atmospheric pressure. Even liquid air may thus be obtained. For this purpose a vacuum jacketed vessel is used. This is a double-walled glass vessel with the air exhausted from the space between the walls. This vacuous space is found to be the best non-conductor of heat. Liquid gases remain quiet in such vessels, evaporating quite slowly, while in ordinary containers they boil away with great rapidity. To obtain liquid air under atmospheric pressure such a vessel is filled with liquid oxygen and closed with a rubber cork through which passes a long test-tube and a small tube which can be con-

Fig. 87.

nected with an exhaust-pump. Upon exhaustion the liquid **oxygen** boils rapidly, temperature goes down to about − 200°, and drops of liquid air collect in the test-tube.
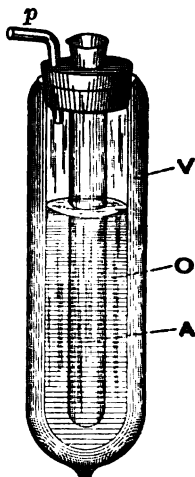
Liquefaction by Pressure and Cold.—By surrrounding the vessel containing the gas to be liquefied by these refrigerating agents and at the same time connecting it with a condensing-pump, conditions of cold and pressure are obtained which no gas can resist. Not only are the gases all liquefied, but all have been obtained in the solid state.

Critical Constants.—If a gas is subjected to increasing pressure, it contracts according to Boyle's law until liquefaction begins. The pressure then remains constant and the volume diminishes until all the gas becomes liquid, when the pressure rises rapidly and the volume undergoes but little more change. As the temperature rises, liquefaction begins at a higher point and the change of volume during liquefaction diminishes, until a temperature is reached at which no liquid is formed. This temperature—that is, the temperature above which a gas will not liquefy—is called the *critical temperature*. The pressure required to liquefy the gas at or just below the critical temperature is the *critical pressure*. The density and volume of the gas under the critical conditions are

called the *critical dens*
critical temperature and

	Nitrogen.	Oxy
Crit. temp....	−146°	−1
Crit. pres.....	35 at.	51

The critical pressure is
in the case of water, a
less than the critical pr
  The diagram, after
under increasing pres
ical temperature is 3
pheres. The abscissa
sure in atmospheres.

150

125

PRESSURE IN ATMOSPHERES

100

7
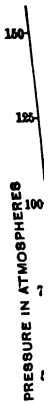
Fig.

Continuity of
heated *above its*
critical pressure, it
just below the cri

same, the gas becomes a liquid, but the change from one state to the other is not observable. Under critical conditions a substance is indifferently a gas or a liquid and the two states are continuous. A sealed tube containing carbon dioxid under its critical pressure will illustrate this phenomenon. '

<div align="center">THE PHASE RULE.</div>

Professor J. Willard Gibbs of Harvard University made a study of the conditions of equilibrium between the solid, liquid, and gaseous states, and discovered an important law which he called the *Phase Rule.* The states are called *phases,* and most substances exist in the three phases, solid, liquid, and gas. Some have four phases; as monoclinic, octahedral, liquid, and gaseous sulfur, while others exhibit a still greater number. Again, the phases are increased when two or more substances or components are present.

Whether these phases exist separately or together depends upon pressure and temperature and the nature of the substance. At the ordinary temperature, iron is wholly solid and hydrogen wholly gaseous, while most liquids and many solids have a certain vapor tension. Alcohol, for example, when confined yields vapor
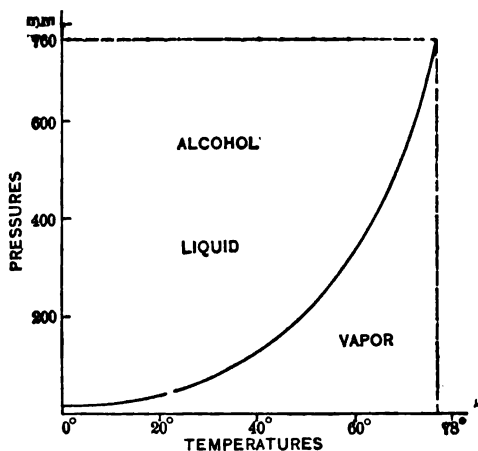
Fig. 39.—Pressure-temperature Curve of Alcohol.

until a certain pressure is reached, then the vapor and liquid remain in equilibrium, or as much vapor returns to liquid as liquid

passes to vapor. If the temperature be raised, more liquid vapor-
izes, and if it be lowered more vapor condenses. There is for
every temperature an equilibrium pressure, and for every pressure
an equilibrium temperature. The figure shows the pressure-
temperature curve of alcohol, which boils at 78° under the atmos-
pheric pressure of 760 millimeters. Each point on the line repre-
sents a certain temperature measured on the horizontal axis and
the corresponding equilibrium pressure measured on the vertical
axis.

The curve represents the conditions of equilibrium between
the liquid and vapor phases. Only liquid can exist above the
curve in stable equilibrium, and only vapor below it.

Here the phases are two and the component one, and there
is one variable and only one degree of freedom; that is, liquid and
vapor can exist together only under conditions represented by
points in the curve.
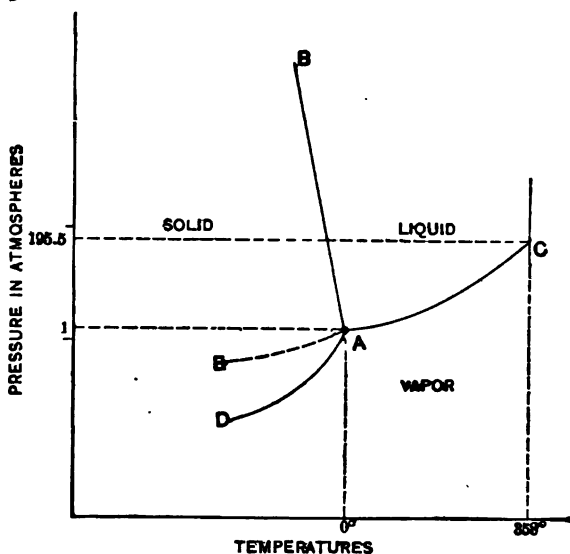
FIG. 40.—Pressure-temperature Curves of Water.

The three phases and the conditions of equilibrium of water
are illustrated in the diagram.

Under the conditions represented by the lines *AB*, *AC* and *AD* the two adjacent phases may coexist in stable equilibrium, but any change of one condition without corresponding change of the other will disturb the equilibrium, and one of the phases will disappear. Here, as in the case of alcohol, there are two phases, one component, one variable, and one degree of freedom.

Within the areas *BAD*, *BAC*, and *CAD*, either temperature or pressure or both may change without changing the phase. There is one component and one phase, while there are two variables and two degrees of freedom.

At the point *A* where the three lines meet, water, ice, and vapor can coexist in equilibrium, but if either pressure or temperature is changed one of the phases will gradually disappear. This is called a *triple point*. There are three phases and one component, no variable and no degree of freedom.

The point *C* represents the critical temperature and pressure and is called the *critical point*. The line beyond this point will be vertical.

Water may be cooled below the freezing-point without becoming liquid; that is, we may have liquid within the area *BAD*. This supercooled water has a pressure-temperature curve which is a continuation of *AC* and is represented by the line *AE*. This condition is an unstable one and is called a *metastable phase*. If a fragment of ice is introduced, the water becomes solid, or the metastable passes to the stable phase. Again, water may be overheated and we may have a metastable liquid phase within the vapor area *DAC*.

All these facts are expressed in the equation

$$P + F = C + 2, \quad \text{or} \quad F = C + 2 - P,$$

in which P = the number of phases, C = the number of components, and F = the degrees of freedom. The equation expresses a generalization which may be interpreted as follows:

1. *If the number of phases exceeds the number of components by two, the system is non-variant, or has no degree of freedom.* The triple point *A* is an example.

2. *If the number of phases exceeds the number of components by one, the system is monovariant, or has one degree of freedom.* The lines *AB*, *AC*, and *AD* are examples.

3. *If the number of phases is equal to the number of components, the system is divariant, or has two degrees of freedom.* The areas *BAC*, *BAD*, and *DAC* are examples.

We may have more than one component, more than three phases, more than two variables, and more than two degrees of freedom, and also a quadruple point, a quintuple point, and so on.

CHAPTER XI.

INTERACTION OF SOLIDS, LIQUIDS, AND GASES.

SOLUTIONS IN GENERAL.

Solutions.—When two substances are brought together, there may be two kinds of action. In the first case they do not mix and there is only a surface action such as is seen in adhesion and capillarity. In the second case there is more or less of mixture, and we have what are called *solutions*.

A solution in the widest sense is an intimate molecular mixture of two or more substances. The one in excess is called the *solvent* and the other the *solute*. In its more common use the word solution indicates the mixture of a solid or a gas with a liquid.

The rapidity of solution and the quantity of the solute dissolved depend upon the temperature, the pressure, the extent of the surface of contact, the amount already in solution, and the nature of the substances. The rapidity of solution is greatly increased by agitation and generally by elevation of temperature.

Coefficient of Solubility.—The *solubility* or *coefficient of solubility* of a substance is the quantity which dissolves in a given quantity of the solvent. For convenience, it is generally reckoned as parts in 100: with solids in liquids, grams in 100 grams; with gases in liquids, volumes in 100 volumes, or cubic centimeters in 100 cubic centimeters.

In stating solubilities it is necessary to mention the temperature. The solubility of oxygen at 0° is about 4 per cent, while at 100° it is zero.

Specific Gravity of Solutions.—When a substance is dissolved in water, or when a solution is diluted, there is a contraction of volume; that is, the resulting volume is less than the sum of the united volumes. The specific gravity of the solution is therefore greater than it would be if the solution were simply a mixture. This contraction in volume has been found to follow certain laws

118

which need not be discussed here. In 100 parts of a solution at a given temperature, there is a definite amount of the solute for each particular density. Specific gravity therefore becomes a convenient means of ascertaining the strength of solutions. Special tables are prepared from which one can read the per cent of the solute corresponding to each degree of gravity.

Dissociation of the Solute.—The character of the solution is modified by the dissociation of the solute. Each ion has the same effect upon the solution as the undivided molecule in many relations, as, for example, upon boiling- and freezing-points. Dissociation increases with the dilution.

Theory of Solution.—The solution theory of J. H. Van't Hoff, a Dutch chemist now at the University of Berlin, as developed by Walther Nernst, University of Göttingen, is based upon the theories of molecular attraction and kinetic energy of moving molecules. At the surface of a solid or a liquid two antagonistic forces are in operation, the one attractive and directed inward, tending to hold the molecules in place, the other directed outward and due to the energy of the moving molecules. When a solid is brought in contact with a liquid which will act upon it, the pressure toward the interior is diminished and the molecules of the solid pass into the liquid. When the liquid has become so filled with the solid that as many molecules return to the solid as leave it, equilibrium results, the solution is saturated, and no more of the solid dissolves. The pressure of the molecules in solution required to balance the pressure at the surface of the solid is called the *solution pressure*. This pressure being exerted only at the surface of contact is independent of the relative quantities of the solid and liquid. It is the measure of the solubility, depends upon the nature of the two substances, and is modified by changes of temperature and pressure.

SOLIDS AND SOLIDS.

Solid Solutions.—The actual solution of solids in solids is seen in mixed crystals of isomorphous substances like the sulfates of magnesium and calcium, in glasses, in the diffused coloring matters of solids, and in alloys. Most of these mixtures are obtained by fusing the substances together, or by allowing them

to crystallize together from solution in water. It has been demonstrated, however, that such solutions may be formed in the cold, and that all solids in contact have a tendency to diffuse into one another. A notable experiment was made by Sir W. Roberts-Austen of London. He placed leaden cylinders upon disks of gold and let them stand for four years. At the end of the time he found by analysis that the gold had penetrated the lead to a depth of eight millimeters. The alloy was richest, of course, at the surface of contact. Another example of the mutual diffusion of metals is seen in the whitening of copper-plated zinc objects due to the passage of the zinc through the copper to the surface.

Properties of Solid Solutions.—Solid solutions possess many of the properties of liquid solutions. They follow, for example, the law of lowering of freezing-point. Alloys melt at a lower temperature than their constituents, and for various metals there is a certain mixture which has the lowest melting-point. This is called a *eutectic alloy.* Good examples are the fusible metals, brass, solder, the gold and silver alloys, and many mixed organic compounds. Solid solutions seem to be formed only by elements that are more or less closely related, and by compounds of like constitution.

SOLIDS AND LIQUIDS.

Solutions of Liquids in Solids.—Solids absorb liquids in various quantities, and it is probable that the mixture is often of the nature of a true solution. Water, for example, not only adheres to the surface, but is found in the interior of most solids. Indeed, it is difficult to obtain free from moisture any substance which is permeable to water.

Solutions of Solids in Liquids.—When a solid comes in contact with a liquid, a portion of it *dissolves*, or forms with the liquid a homogeneous mixture. The solvent most used is water, and aqueous solutions are always meant when the solvent is not named.

Limits of Solubility.—The amount of the solid dissolved by the liquid varies with different substances from an infinitesimal portion to a quantity two or three times the weight of the liquid. Metals like gold, silver, and platinum do not dissolve in water in weighable quantities, but refined physical methods prove that solution does actually take place. Other substances dissolve in

such small quantities that they are also said to be insoluble. The solubility of barium sulfate, for example, is 1 part in 400,000 parts of water. Again, other substances have a high solubility. Water will dissolve at 18° nearly one half its weight of sodium sulfate and more than three times its weight of calcium permanganate.

When the liquid will dissolve no more of the solid, that is, when the solution pressure is counterbalanced, it is said to be *saturated*. When it contains less than the saturating amount, it is *unsaturated*. When a solution is concentrated by evaporation, or when the temperature of a saturated solution is lowered, it may become *supersaturated* before the separation of the solid begins. If a crystal of the dissolved substance be added to a supersaturated solution, or if it be violently shaken, the excess of the solid separates and the solution remains saturated.

Influence of Pressure upon Solubility.—The solubility of solids increases with increase of pressure. The change, however, is very small, no doubt, because neither liquids nor solids suffer any considerable change in volume when the pressure is changed. K. Möller found that common salt dissolved at 0° in 100 parts of water, 35.59 parts at a pressure of one atmosphere, 35.79 parts under 20 atmospheres, and 35.95 parts under 40 atmospheres.

Influence of Temperature upon Solubility.—The solubility of solids generally increases with rise and diminishes with fall of temperature. Some substances are but slightly affected, while others undergo great change of solubility as the temperature rises. The solubility of sodium chlorid, for example, is 35.6 at 0° and 40 at 100°, while that of potassium nitrate is 13 at 0° and 247 at 100°. Sometimes the solubility diminishes as the temperature rises, as in the case of anhydrous sodium sulfate and the calcium salts of some organic acids.

Solubility curves are constructed by laying off the temperatures on the horizontal axis and the solubilities in parts to the hundred on the vertical axis.

The curves are generally continuous and often rectilinear. Some substances give two or more intersecting curves. These represent different conditions of the substance. The curve of sodium sulfate in the diagram is an example. Below 33° it represents the compound $Na_2SO_4,10H_2O$, while above that point the

compound in solution is anhydrous Na_2SO_4. At 33° the hydrous salt loses its water of crystallization.

Osmotic Pressure.—When a solution is brought in contact with the pure solvent or with a more dilute solution, the dissolved .
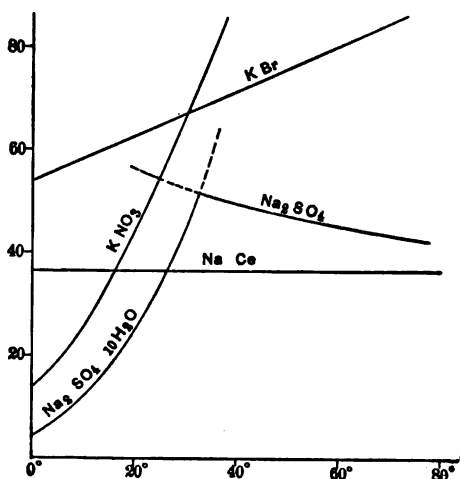
FIG. 41.—SOLUBILITY CURVES.

substance will move toward the points of less concentration, and the movement will continue until the whole solution is homogeneous. If the movement is hindered by the introduction of a partition or membrane, permeable by the solvent but not by the solute, a pressure will be exerted against the partition. This is called *osmotic pressure* and the partition is said to be *semi-permeable*.

The laws of osmotic pressure were first investigated in 1877 by W. Pfeffer, a German botanist of Leipzig. He used an artificial membrane prepared after a method discovered by Moritz Traube of Breslau. Porous earthenware cells were filled with a solution of potassium ferrocyanid and immersed in a solution of copper sulfate. The solutions meeting in the cell wall react to form a delicate film of copper ferrocyanid. This film is so supported by the wall of the cell as to be able to resist great pressure. After the film is formed, the cell is washed clean and filled with the solution to be tested. It is closed, connected with a manometer, and im-

mersed in pure water. The water can pass in through the film, but the solute cannot pass out. There is therefore produced a pressure within the cell which is measured by the manometer.

Some of Pfeffer's results and the inductions which come legitimately from them are given.

One per cent solutions gave mercury pressures as follows:

Gum . . . . 72 millimeters   Cane-sugar . . . 471 millimeters
Dextrin. 166   "   Nitre. 1780   "

Therefore: *Osmotic pressure depends upon the nature of the solute.*

Sugar solutions of various strengths gave these results:

Per cent.	1	2	4	6
Pressure in millimeters.	532	1016	2082	3075
Pressure per cent.	532	508	521	513

Therefore: *The pressure varies directly as the concentration.*

One per cent solutions of sugar at various temperatures gave the following:

6.8° . . . . 505 millimeters   14.2° . . . . 531 millimeters
13.2° 521   "   22.0° 548   "

Therefore: *As the temperature rises the pressure rises.*

If we reduce these temperatures to absolute temperature by adding 273° to each, and then divide the pressure by the temperature, we obtain the constant quotient 1.8.

Therefore: *The pressure varies directly as the absolute temperature.*

If solutions of two substances yield the same osmotic pressure, they are said to be *isotonic.* A series of investigations made by H. de Vries of Amsterdam, based upon the action of solutions upon vegetable cells, led to the conclusion that *isotonic solutions of similar compounds contain the solutes in the proportion of their molecular weights.*

The reciprocal of the gram-molecular content of a solution is called its *isotonic coefficient.* Some of these coefficients found by de Vries are as follows:

Glycerin, $C_3H_8O_3$, ... 1.78   Potassium nitrate, KNO_3. . . . . . 3.00
Grape-sugar, $C_6H_{12}O_6$ . . . . 1.81   Sodium chlorid, $NaCl$. 3.05
Tartaric acid, $C_4H_6O_6$. . . . . 2.02   Potassium sulfate, K_2SO_4 . . . . . 3.92
Citric acid, $C_6H_8O_7$ . . . . 2.02   Potassium tartrate, $K_2C_4H_4O_6$. . 3.99
Potassium citrate, $K_3C_6H_5O_7$. . . . 5.01

These numbers show that the isotonic coefficients are the same for similar compounds, and that for different classes of compounds they are approximately whole numbers proportional to the numbers 2, 3, 4, and 5. These variations are explained by the theory of dissociation, and the law still holds that *equimolecular solutions are isotonic;* that is, solutions which contain in the same volume of water the solutes in the proportion of their molecular weights or ionic equivalents will exert equal osmotic pressures.

Molecular Weight from Osmotic Pressure.—Molecular weight may be computed from osmotic pressure as follows: A 1 per cent solution of sugar contains 10 grams to the liter and has an osmotic pressure of 49.3 centimeters of mercury. If the solution were normal the pressure would be $22.24 \times 76 = 1690$ centimeters. We therefore have the proportion

$$49.3 : 1690 :: 10 : M, \text{ or } M = 342.8.$$

The molecular weight of sugar is 342. This determination shows also that the molecule is single in the solution.

Osmotic Pressure and the Gas Laws.—The principal laws of osmotic pressure may be stated as follows:

1. The pressure varies directly as the concentration in a given volume, or inversely as the volume which contains a given quantity of the solute.

2. The pressure varies for constant volume directly as the absolute temperature.

3. Gram-molecular weights or gram-ionic weights of substances dissolved in equal volumes of water exert equal pressures at equal temperatures.

In 1887 Van't Hoff suggested the close analogy between these laws and the laws of gases. The first corresponds to the law of Boyle and is expressed by the equation

$$pv = p'v' = \text{a constant,}$$

in which p and p' are pressures and v and v' volumes containing the same amount of the solute.

The second statement is analogous to the law of Gay-Lussac, and the equation

$$p = p_0(0.003665t)$$

is true when $p=$ the pressure at temperature t and $p_0=$ the pressure at $0°$; or in terms of absolute temperature,

$$p=cT(c=\text{a constant}).$$

Combining these two laws we have, as with gases,

$$pv=\frac{p_0v_0}{273}T=RT.$$

In this equation the value of R may be calculated. A 1 per cent solution of sugar exerts an osmotic pressure at $0°$ of 49.3 centimeters of mercury, which is equal to $49.3\times13.59=670$ grams per square centimeter. The molecular weight of sugar is 342, and therefore a 1 per cent solution containing 342 grams will have a volume of 34,200 cc. The value of R then is

$$R=\frac{670\times34200}{273}=83,930 \text{ gram-centimeters}.$$

This number corresponds very closely to the value of R for gases, 84,760, and the equation may be written

$$pv=84,000T.$$

Since, according to the third law above, equimolecular solutions exert the same pressure, the following law is proven:

The osmotic pressure of a dissolved substance is equal to the pressure which it would exert as a gas occupying the volume of the solution. The pressure would remain the same if the solvent were removed, leaving the solute unchanged.

The similarity between gaseous and dissolved substances is of great importance, for we are able to apply to solutions the properties of gases so far as they are dependent upon pressure, volume, and temperature. We may conclude, for example, that *isotonic solutions contain in the same volume the same number of molecules.* We can therefore ascertain the molecular weight of dissolved solids.

Osmotic pressure reaches heights which are very surprising. In a normal solution it is about 22 atmospheres, and in a 17 per cent solution of ammonia it is no less than 222 atmospheres. This

number may be computed from the last equation above. Since the molecular weight of ammonia is 17, a 1 per cent solution containing 17 grams would have a volume of 1700 cc., and a 17 per cent solution 100 cc. The atmospheric pressure is 1033 grams to the square centimeter. The equation then becomes

$$v = \frac{83930 \times 273}{100 \times 1033} = 222 \text{ atmospheres.}$$

The same number may be obtained otherwise. A mol. of gas under standard conditions occupies a volume of 22.24 liters. At a volume of 1 liter it will therefore have a pressure of 22.24 atmospheres. This is also the osmotic pressure of a mol. of a solid dissolved in 1 liter; that is, in normal solution. A 17 per cent solution of ammonia is ten normal, and will have a pressure ten times as great, or 222.4 atmospheres.

The question naturally arises, How can such enormous pressures exist without making themselves manifest? In the laboratory reagent bottles the pressure is fifty atmospheres, more or less. Why are the bottles not broken? They would be if they were pervious to and immersed in water. The osmotic pressure cannot appear at the surface of a liquid, because it is more than balanced by the pressure towards the interior, which is manifested in surface tension and is measured in thousands of atmospheres. The semipermeable membrane, having the solvent on both sides and the solute only on one side, enables the pressure of the solute to become manifest.

Diffusion.—Osmotic pressure always exists when a solution is in contact with the solvent, though no membrane intervenes. If a colored solution be placed in a cylinder and covered with pure water, the color will gradually rise until it is uniform throughout the cylinder. If two solutions be placed one above the other, the one solute will move up and the other down until the mixture is homogeneous. This movement is called *diffusion,* and is always from the point of greater to the point of less concentration. It was first observed by Parrot in 1815, and afterwards investigated by Graham in 1851, by Fick in 1855, by Beilstein in 1856, by Weber in 1879, by Long in 1880, by Nernst in 1888, and by many others.

Rate of Diffusion.—Diffusion takes place very slowly because of the great resistance which the solute has to overcome in moving

through the solvent. It was calculated by Nernst that the force necessary to drive a gram-molecular weight of cane-sugar through water with a velocity of 1 centimeter a second is 6700 million kilograms, and that for albumen the force required is five times as great. Ostwald explains that this enormous resistance is due to the multitude of molecules. A stone acted upon by gravity falls 980 centimeters in a second, but if it were ground to a fine powder, its velocity would be reduced to less than one tenth of a centimeter in a second. To make it move in the state of dust with the velocity of the falling stone, would require a force ten thousand times that of gravity. We can thus understand how the resistance can be so great when the body is in the molecular state.

Careful investigations of the rate of diffusion were made by Graham, Beilstein, and Weber. Thomas Graham, a British chemist, filled a glass jar to within 2 centimeters of the top with the solution, then carefully added water until the jar was full. He placed the jar in another vessel and completely covered it with water. After the lapse of one or more days, he closed the jar with a glass plate and removed it. He then determined the quantity of the solute which was contained in the water in the vessel. By this means he was able to arrive at the following conclusions:

1. The rate of diffusion depends upon the nature of the substance. Acids and bases diffuse twice as rapidly as salts and salts more rapidly than many organic compounds.

2. The rate of diffusion is proportional to the quantity of solute present; that is, to the concentration.

3. The rate of diffusion is modified by change of temperature, generally rising as the temperature rises.

4. When two or more solutes are present, they diffuse independently. If the rate of two salts is quite different, they can be separated by diffusion.

The first of these conclusions was expressed by A. Fick in the following form: *The quantity of a salt which diffuses through a given area is proportional to the difference between the concentrations of two areas infinitely near one another.* This law is known as *Fick's law of diffusion,* and has been verified by numerous experiments.

Crystalloids and Colloids.—There are many amorphous sub-

stances which diffuse very slowly, while crystalline salts generally diffuse rapidly. The former are called *colloids* and the latter *crystalloids*. Crystalloids dissolve in water with heat changes, raise the boiling-point, lower the freezing-point, and exert osmotic pressure; while colloids possess these properties in a much lower degree or not at all. Colloidal membranes are impervious to colloids, but give free passage to crystalloids. If a solution containing a colloid and a crystalloid be separated from pure water by a colloidal membrane, such as bladder or parchment paper, the former will diffuse through while the whole of the latter will be retained. Such separation was called by Graham *dialysis*.

Colloidal substances are liable to separate from solution in a coagulated or gelatinous and insoluble form. This precipitation usually takes place spontaneously in course of time, but it may be brought about at once by action of catalytic agents. The colloidal solution is rather a mixture than a true solution, and many substances which are insoluble in water, such as the metals, may be brought into *colloidal solution*.

Vapor Pressure of Solutions.—The vapor pressure of a solution is lower than that of the solvent, provided the solute has not an appreciable vapor pressure. The investigations of von Babo in 1848 and of Wüllner in 1856 led to the conclusion that *the diminution of vapor pressure in a solution is proportional to the concentration, or to the amount of the solute present.* Let p be the vapor pressure of the solvent, p' that of the solution, s the percentage of the solute, and a the relative depression for a 1 per cent solution, then

$$\frac{p-p'}{p} = as.$$

To this law there were many exceptions, but these have been explained by the dissociation theory. The solvent used was water and the solutes were salts, conditions highly favorable to dissociation.

François Marie Raoult, about 1887, using ether as the solvent for organic substances which do not dissociate, obtained results which are highly concordant. He found in the first place that between 0° and 20° the ratio of the vapor pressure of solvent and solution was constant; that is, *that the relative depression was independent*

of the temperature. This is evidenced by the following results, which were obtained by measuring the pressures at different temperatures, of a solution of 16.482 grams of oil of turpentine in 100 grams of ether, p being the vapor pressure of the solvent, p' that of the solution, and t the temperature:

$t=1.1°$	$p=199.0$	$p'=188.1$	$p'\div p=0.915$
$t=3.6°$	$p=224.0$	$p'=204.7$	$p'\div p=0.914,$
$t=18.2°$	$p=408.5$	$p'=368.7$	$p'\div p=0.910$

Raoult showed in the second place that if a gram-molecular weight of any substance is dissolved in a given weight of a particular solvent, the same lowering of vapor pressure is produced; that is, *the molecular lowering is constant for each solvent.* He found also that with different solvents, *the relative lowering of the vapor pressure is proportional to the ratio of the number of molecules of the solute to the sum of the molecules of the solute and solvent;* or that

$$\frac{p-p'}{p}=c\frac{n}{N+n},$$

when $n=$ the number of molecules of the solute, $N=$ the number of molecules of the solvent, and $c=$ a constant which was found to be nearly equal to one.

This equation serves for the determination of molecular weights. Let $m=$ the unknown molecular weight of the dissolved substance, and $w=$ the weight dissolved in one molecular weight of the solvent, then $n=\dfrac{w}{m}$ and $N=1$, and c may be taken as equal to 1. After substituting and solving for m, the equation becomes

$$m=\frac{wp'}{p-p'}.$$

This method of determining molecular weight does not admit of great accuracy because of the difficulty of measuring vapor pressure, and has been replaced by the boiling-point method.

Boiling-point of Solutions.—Instead of determining the vapor pressure of solutions at different temperatures, Ernst Beckmann of Giessen ascertained the temperature at which solvent and solution have the same pressure, that is, the boiling-point. Since the

pressure of a solution is lower than that of the solvent, the boiling-point will be correspondingly higher. It follows, therefore, that the rise of boiling-point will follow the same laws that we have found to apply to vapor pressure. A gram-molecular weight of any substance dissolved in a definite weight of a solvent, say 100 grams or 100 mols., will cause a constant rise of the boiling-point, which may be determined for each solvent. For example, 1 mol. of a substance dissolved in 99 mols. of ether causes a rise of 0.2844°. One hundred times this, 28.44°, is the molecular rise for ether.

The molecular constant is usually determined for a solution of 1 mol. of the solute in 100 grams of the solvent. Some of the molecular constants are as follows: Water, 5.2; benzene, 26.7; chloroform, ·36.6; carbon disulfid, 23.7; ether, 21.1; alcohol, 11.5.

Molecular Weight by Boiling-point.—If we let $R =$ the observed rise for a 1 per cent solution and $M =$ the molecular weight of the solute, then $MR = C$, the molecular constant for the solvent, and the molecular weight will be determined by the equation $M = \dfrac{C}{R}$. If w grams of the solute are dissolved in W grams of the solvent, and the observed rise is r, the molecular rise will be

$$R = \frac{rW}{100w} \quad \text{and} \quad M = \frac{100Cw}{rW}.$$

Example.—Beckmann dissolved 1.065 grams of iodin in 30.14 grams of ether and observed a rise of 0.296. The constant for ether is 21.1. Making the substitutions we have

$$M = \frac{100 \times 21.1 \times 1.065}{0.0296 \times 30.14} = 252.$$

The formula I, corresponds to the molecular weight 253.7.

Boiling-point Determinations.—The apparatus used by Beckmann for boiling-point determinations was rather complicated. A simpler one, devised by Herbert N. McCoy of the University of Chicago, is shown in the figure. The inner tube A has a side outlet c, connected with a condenser, and a small tube v, entering at a and extending to near the bottom. The tube is graduated and carries a Beckmann thermometer. The outer tube B is enlarged at the bottom, and has a side tube d, closed with a rubber tube and pinch-clamp.

The Beckmann thermometer has a large bulb and a reservoir at the top of the stem into which the excess of mercury can be driven by warming the bulb. A small portion of the stem is graduated into degrees, tenths, and hundredths, and with a lens the reading may be taken to thousandths. The amount of mercury in the bulb is so adjusted by shaking that the top of the column is within the range of the graduation, which is usually 6°.

A determination is made as follows:

About 50 cc. of the solvent are placed in the outer tube (with some fragments of pipe-stem to prevent bumping), and 15 cc. in the inner tube. As the liquid in the outer is boiled, the vapor passes through the tube *ab*, heats the liquid within to boiling, and the excess of vapor passes out through *c*. Superheating is thus avoided. When the mercury ceases to rise the reading is taken and represents the boiling-point of the solvent. As the apparatus cools, the pinch-clamp must be opened to prevent suction of the liquid out through *ab*. A weighed quantity of the substance is added to the inner tube and the operation repeated. The reading is now the boiling-point of the solution, and the difference between the two readings is the rise of the boiling-point. The thermometer is removed, the volume of the solution is read from the graduated tube, and its concentration calculated.

Freezing-point of Solutions.—It has long been known that the freezing-point of a solution is below that of the solvent. As early as 1788 Sir Charles Blagden showed that the depressions of the freezing-point were proportional to the quantities of the substance in solution. He also showed that when two substances are present in the solution the depression is equal to the sum of the depressions which would be caused by each substance alone. These laws are now known not to be rigidly true, but they were a great
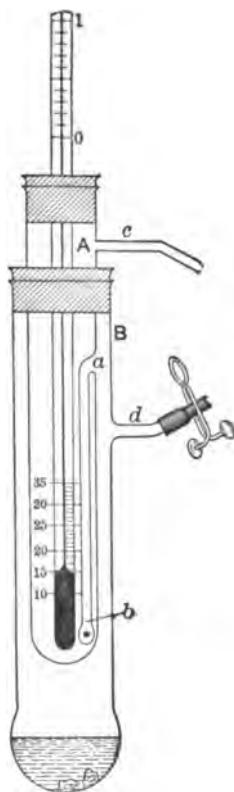
Fig. 42.—McCoy's Boiling-Point Apparatus.

discovery, which was for a long time forgotten. In 1861 **Rüdorff** made the same discovery without knowing of Blagden's work.   In 1872 Coppet continued the investigation, using molecular quantities instead of percentages. He introduced the term *molecular lowering of the freezing-point*, and showed that this is constant for many substances.

About 1882 Raoult began a series of investigations which were epoch-making. He examined solutions of more than two hundred substances in various solvents. He determined the molecular lowerings for various solvents, and found that if these were divided by the molecular weights of the solvents, the quotients were equal. The following are some of his results:

Solvent.	Molecular Weight.	Molecular Low.	M.L.÷M.W.
Water.	18	47	2.61°
Formic acid.	46	29	0.63°
Acetic acid.	60	39	0.63°
Benzene	78	60	0.64°

From these results Raoult formulated the law as follows:

If one molecule of a substance is dissolved in 100 molecules of a liquid, the lowering of the freezing-point is constant and approximately equal to 0.63°.

In the above table water does not follow the law. This is explained by supposing that the molecule of water is complex and that its formula is $4H_2O$. Other considerations also point to this formula for water.

Using *molecular depression* to mean that of a solution of 1 mol. of a solute in 100 grams of a solvent, some of the constants are as follows: Water, 18.9; formic acid, 27.7; acetic acid, 39; benzene, 50; carbolic acid, 75.

Freezing-point Determinations. — The determination of the freezing-point of solutions may be made with the simple apparatus devised by J. F. Eykman of Groningen, and called by him the *depressimeter*.   A short thermometer divided to twentieths of a degree is fitted into a small flask, as shown in the figure. Both are enclosed in a cylinder and held in place by means of the stopper through which the thermometer-tube passes.   Glass or cotton-wool

at the bottom of the cylinder regulates the cooling. A weighed quantity of the solvent is placed in the flask and its freezing-point determined. Weighed portions of the solute, making solutions from 1 to 10 per cent are added, and the freezing-point determined after each addition. The depression for the 1 per cent solution is obtained by interpolation. By using a diagram in which the abscissas represent the concentrations and the ordinates 'the depressions, the depression · for infinite dilution is obtained by exterpolation.

Molecular Weight by Freezing-point.—The freezing-point like the boiling-point affords a means of determining molecular weight. Let $D=$ the depression observed for a 1 per cent solution and $M=$ the molecular weight of the solute, then $MD=C$, the molecular constant for the solvent, and the molecular weight $M=\dfrac{C}{D}$.

Example.—A solution of 0.68 gram of acetic acid in 100 grams water caused a depression of 0.2168. The depression for a 1 per cent solution would be $D=0.2168\div0.68$, and since for water $C=18.9$, the above equation becomes

$$M=\frac{18.9\times0.68}{0.2168}=59.3.$$

FIG. 43.—DEPRESS-IMETER OF EYK-MAN.

The molecular weight of acetic acid is 60.

Dissociation by Freezing-point.—An ion causes the same depression as a molecule, and therefore solutions of electrolytes will have abnormally low freezing-points and the molecular weight found will be too small. This fact may be used for determining the percentage of dissociation of the electrolyte. The increase in depression will be proportional to the increase in number of ions and molecules and the total number of these, i, will be found by dividing the molecular depression found, m, by the normal depres-

sion for the solvent. For water, $i = \frac{m}{18.9}$. If $a =$ the number of molecules decomposed in 100, $2a =$ the number of ions formed when the electrolyte is binary, $1 - a =$ the number of molecules not decomposed, and

$$i = (1 - a) + 2a = 1 + a, \quad a = i - 1.$$

Example.—A 0.0107 normal solution of potassium hydroxid gave a depression of 0.0388. The molecular depression was therefore $\frac{0.0388}{0.0107} \times 100 = 36.3$, and $i = \frac{36.3}{18.9} = 1.92$. Hence, $a = 1.92 - 1 = 0.92$, or the dissociation was 92 per cent.

Freezing-point and Hydrates.—Since dissociation grows less as the solution grows stronger, we should expect that as the concentration increases the molecular lowering would decrease to a minimum and then remain constant. An investigation begun in 1900 by Harry C. Jones of Johns Hopkins University showed that with increasing strength of solutions the molecular depression generally falls to a minimum and then rises, sometimes quite rapidly, and often reaches heights above those which correspond to complete dissociation. Jones explains this abnormal depression by supposing that hydrates are formed and that the number of molecules of water combining with one molecule of the solute increases with the concentration. The water thus combined acts no longer as the solvent and does not influence the freezing-point, and the solution is really more concentrated than it seems.

The number of molecules of water contained in one molecule of the hydrate varies from one to fifty or more. The following are examples: Copper chlorid, normal, 20 molecules, twice normal, 35 molecules; aluminum chlorid, one fifth normal, 3 molecules, one half normal, 19 molecules, normal, 36 molecules, and twice normal, 48 molecules. It was found that salts which contain water of crystallization form the hydrates with much water.

SOLIDS AND GASES.

Solutions of Solids in Gases.—Many solids in contact with gases give off vapor which mixes with the gas and may be regarded as a solution of the solid in the gas. Iodin and camphor are good examples. As the temperature rises the solubility increases. Since the solid passes to the gaseous state, the result is really a solution of gas in gas.

Solutions of Gases in Solids.—Many solids dissolve gases, sometimes in large quantities. Charcoal will absorb 90 times its volume of ammonia and 35 times its volume of carbon dioxid. The quantity dissolved increases with the pressure and may increase or decrease with the temperature.

LIQUIDS AND LIQUIDS.

Solutions of Liquids in Liquids.—Some liquids mix in such small quantity that they are said to be mutually insoluble. An example is oil and water. Other liquids dissolve one another to a limited extent. For example, ether dissolves in water and water in ether, but if more than one part of ether is added to ten parts of water, or more than three parts of water to one hundred parts of ether, the excess forms a separate layer and each liquid is saturated with the other. Still other liquids mix in all proportions; as alcohol with water and chloroform with carbon disulfid.

The properties of liquid solutions are not the sum of the properties of the separate liquids. There is generally contraction of volume, change of vapor pressure and of boiling-point, and increase of solubility with rise of temperature. There is usually development of heat when the liquids are mixed, but sometimes heat is absorbed.

Boiling-point and Vapor Pressure of Mixed Liquids.—With mixed liquids three cases may arise:

1. When the liquids do not mix, each gives off its normal amount of vapor and the pressure is equal to the sum of the partial pressures of the several vapors. In this case the mixture boils at

a lower temperature than either of the constituents. Bromoform (CHBr₃) boils at 151°, but if water be poured upon it, the boiling begins at the surface between the liquids at 93°, this being the temperature at which the sum of the partial pressures is equal to the pressure of the atmosphere.

2. When the liquids mix only to a limited extent, the vapor pressure is less than the sum of the partial pressures and generally is only equal to that of the more volatile constituent. A mixture of water and ether boils at 35°, the boiling-point of ether. The boiling continues at about this temperature until the ether has all passed over, then ceases until the boiling-point of water is reached.

3. When the liquids mix in all proportions, the vapor pressure is even less than that of the more volatile constituent, and lies somewhere between the several partial pressures, being nearer to that of the liquid present in the larger proportion. Upon distillation the lighter liquid comes off rapidly at first and the boiling-point gradually rises until it approaches that of the heavier liquid. The first portion of the distillate consists largely of the more volatile liquid, while the last portion contains the heavier one. By collecting in separate portions and repeating the distillation the liquids may be completely separated. This process is called *fractional distillation.* Two liquids which have the same boiling-point cannot, of course, be separated in this way.

Mixtures with Constant Boiling-point.—There are some liquid mixtures which show a maximum of vapor pressure or a minimum of boiling-point. A mixture of propyl alcohol and water has its lowest boiling-point when it contains 70 per cent of the alcohol and 30 per cent of water. So also there are mixtures which have a minimum of vapor pressure or maximum of boiling-point. Formic acid and water is such a mixture and has the highest boiling-point when there is present 25 per cent of water. Such mixtures cannot be separated by distillation. The distillate will vary in composition until the maximum or minimum boiling-point is reached and then will contain the two substances in constant proportion until the liquid is all boiled away. A mixture of hydrochloric acid and water, for example, containing 20.2 per cent of hydrogen chlorid distils unchanged at 110° under atmospheric pressure. A stronger acid grows weaker and a weaker acid grows stronger, when distilled, until the above strength is reached.

Roscoe showed that these mixtures are not chemical compounds by establishing the fact that the composition of the distillate changes with the pressure.

LIQUIDS AND GASES.

Solutions of Liquids in Gases.—When a liquid is in contact with a gas, it gives off vapor until the gas is saturated. This may be said to be a solution of the liquid in the gas. It does not differ, however, from ordinary evaporation, since the vapor pressure of a liquid in contact with a gas seems to be the same as in a vacuum.

Solutions of Gases in Liquids.—When a gas is brought in contact with a liquid it is absorbed until the liquid is saturated. The volume of the gas absorbed by one volume of the liquid is called the *solubility*, or *coefficient of solubility*, of the gas. This coefficient varies between large limits, being 0.02 for nitrogen and 1100 for ammonia.

There are two classes of gas solutions. In the first class there is no chemical action and the gas is completely expelled by raising the temperature to the boiling-point of the liquid or by reducing the pressure to zero. These are the true solutions and the ones to which the laws of gas solutions apply. In the second class there is chemical union between the gas and the liquid, and the gas is not all expelled under the above conditions. These are called *chemical solutions*, and to them the laws of gas solutions do not strictly apply.

The amount of a gas which dissolves in a liquid depends upon various conditions, the most important of which are as follows:

1. *The Nature of the Two Substances.* — Gases are generally more soluble in alcohol than in water and the solubility is generally low where there is no chemical action. The following table illustrates the wide range of solubility. W is the coefficient of solubility in water, and A in alcohol at 0° and 760 mm.

	W.	A.		W.	A.
Nitrogen	0.020	0.126	Carbon monoxid	0.033	0.204
Hydrogen	0.019	0.069	Hydrogen sulfid	4.371	17.890
Oxygen	0.041	0.284	Hydrogen chlorid	503	
Carbon dioxid	1.797	4.329	Ammonia	1100	

2. *The Temperature.*—The solubility diminishes as the temperature rises, slowly in true solutions, more rapidly in chemical

solutions. At the boiling-point the gas is completely expelled from true solutions and in some cases from chemical solutions. The following table shows the effect of rise of temperature upon solubility:

	N	CO_2	H_2S	HCl	NH_3
0°	0.020	1.797	4.371	503	1148
10°	0.016	1.185	3.586	450	865
20°	0.014	0.901	2.905	425	654
50°	0.008	0.500	2.000	364	306
100°	0.000	0.000	0.000	12	0

3. *The Pressure—Henry's Law.*—Experiments made by William Henry in 1803 and verified by Bunsen established what is known as *Henry's law*, viz., The quantity of a gas dissolved by a definite quantity of a liquid is proportional to the pressure of the gas. Since the volume of a gas is inversely proportional to the pressure, the law may be stated thus: *A given quantity of a liquid dissolves the same volume of a gas at all pressures.*

The following table gives the volume of carbon dioxid which dissolves in unit volume of water at different pressures and the ratio of the two volumes. The last is seen to be practically constant:

p	v	$p+v$	p	v	$p+v$
80.9	1.1619	0.01352	218.9	3.1764	0.01452
147.0	2.1623	0.01471	255.4	3.7152	0.01455

Some gases, particularly those which have a high solubility and act chemically with the solvent, show deviations from Henry's law. Ammonia and sulfurous oxid are examples. These, however, at higher temperatures—ammonia at 100°, and sulfurous oxid at 40°—follow the law.

Solutions of Gases in Gases.—Gases expand indefinitely and always fill the vessel which contains them. If two vessels containing different gases be brought mouth to mouth, they will soon both be filled with a mixture of the two gases. If a porous plate be interposed, the gases will pass through it. This mutual mixing of gases is called *diffusion,* and is due to the continuous motion of the gaseous molecules.

Law of Diffusion.—The law of diffusion is determined by experiment, but may also be derived in accordance with the kinetic theory of gases. All gases sustain the pressure of the atmosphere, and equal volumes contain the same number of molecules. Since

pressure is the result of molecular impact, the lighter molecules must move more rapidly than the heavier ones in order to strike with the same force. According to physical laws impact is equal to the mass multiplied by the square of the velocity. Since pressure represents impact and mass is proportional to density, we have

$$p = dv^2 \quad \text{and} \quad p = d'v'^2,$$

whence

$$dv^2 = d'v'^2 \quad \text{and} \quad d = \frac{d'v'^2}{v^2}, \quad \text{or} \quad v = v'\sqrt{\frac{d'}{d}},$$

in which p is the atmospheric pressure, d and d' the densities, and v and v' the diffusion velocities of two gases. If d and d', representing the density and velocity of hydrogen, be taken as unity, we have

$$d = \frac{1}{v^2} \quad \text{and} \quad v = \frac{1}{\sqrt{d}}.$$

Hence the law: *The density of a gas varies inversely as the square of the velocity of diffusion, and the velocity of diffusion varies inversely as the square root of the density.*

Since there is a fixed relation between density and molecular weight, diffusion becomes a means of confirming molecular and atomic weights.

Illustration.—Close a porous earthenware cup with a cork through which passes a long glass tube; support it upright with the end of the tube dipping in water. Lower over the cup a vessel of hydrogen. The hydrogen diffuses into the cup faster than the air diffuses out and the excess bubbles out below. Remove the vessel and now the hydrogen diffuses out faster than the air diffuses in and the water is drawn up into the tube.

Properties of Gas Solutions.—The properties of solutions of gases in gases are the sum of the properties of the constituents. The total pressure is equal to the sum of the partial pressures. The law of Boyle applies, and

$$pv = p_1v_1 + p_2v_2 + p_3v_3 \dots,$$

or the product of the total pressure and volume is equal to the sum of the products of the partial pressures and volumes.

Deviations from this law have been observed. When gases are mixed under high pressure, there is sometimes an increase and sometimes a decrease of volume.

CHAPTER XII.

THERMOCHEMISTRY.

Energy Changes.—Chemical changes involve energy changes. Every chemical action is attended by certain physical energies which may take the form of heat, light, electricity, sound, or mechanical work. This energy is generally liberated as heat and in many cases can be wholly transformed into it. Heat is then taken as the measure of chemical energy, but it must be remembered that this physical energy may not and probably does not include the whole of the energy of chemical actions. The study of the thermal effects of chemical changes is called *thermochemistry*.

Thermal Equations.—The ordinary chemical equation indicates molecular and weight changes, but ignores the attendant development and transformation of energy. The equation $H_2 + Cl_2 = 2HCl$ tells us that two grams of hydrogen and 71 grams of chlorin unite to make 73 grams of HCl, but says nothing of the fact that there is at the same time liberated enough heat to raise 44,000 grams of water through one degree of temperature. The equation is made to indicate this new fact by a simple addition thus:

$$H_2 + Cl_2 = 2HCl + 44,000 \text{ cal.},$$
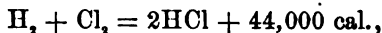
cal. meaning gram-calories. Another method of writing the equation is this:

$$[H_2, Cl_2] = 44,000.$$
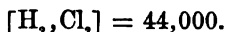
This equation is reversible and may be written

$$2HCl = H_2 + Cl_2 - 44,000 \text{ cal.},$$
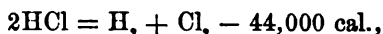
ꞁich means that in the decomposition of 73 grams of HCl into and Cl there are absorbed 44,000 heat-units.

140

A reaction in which heat is liberated is called *exothermic,* and compounds thus formed are stable.

A reaction in which heat is absorbed is called *endothermic,* and the compounds formed are unstable.

Heat developed is indicated by the plus sign, heat absorbed by the minus sign.

In thermal equations molecular formulas are used and molecular quantities in grams are always meant. Practically it is more convenient to have the equations in their lowest terms, and they will be so used. The reaction above may as well be written

$$H + Cl = HCl + 22,000 \text{ cal.}$$
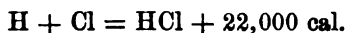
The thermal effects of chemical action are not so simple as they would at first appear. There are many attendant conditions which influence the results. Some of them are as follows:

1. *Molecular condition of the factors.* In the formation of HCl the thermal equivalent, 44,000 cal., is not the full measure of the heat developed in the action, but the difference between this heat and that consumed in the decomposition of the molecules of hydrogen and chlorin.

2. *The physical state of the factors and products.* If in the reaction the state of either substance is changed, there is a corresponding change in the thermal effect. The equation for the synthesis of water as steam is

$$H_2 + O = H_2O \text{ (steam)} + 58,690 \text{ cal.}$$

In the condensation of steam heat is evolved as follows:

$$H_2O \text{ (steam)} = H_2O \text{ (water)} + 9670 \text{ cal.}$$
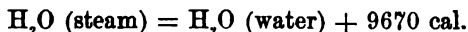
The equation, then, for the synthesis of water in its liquid form is

$$H_2 + O = H_2O \text{ (water)} + 68,360 \text{ cal.}$$

The physical state is indicated, when desirable, by using heavy-faced type for solids, italics for gases, and ordinary type for liquids. Example:

$$\mathbf{C} \text{ (solid)} + Cl_4 \text{ (gas)} = CCl_4 \text{ (liquid)} + 21,000 \text{ cal.}$$
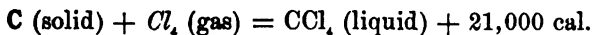
3. *The presence of water.* Many substances unite with water or dissolve in it with thermal changes. The molecular quantity

of water is indicated by the formula H_2O; an excess of water, such that the addition of more produces no thermal change, is indicated by the symbol Aq. Take for example the formation and solution of hydrobromic acid:

Formation . . . . $H + Br \text{ (gas)} = HBr \text{ (gas)} + 12,100$ cal.
Solution in water. . . . . . . $HBr + Aq = HBrAq + 19,900$ cal.
Formation and solution . . $H + Br + Aq = 32,000$ cal.
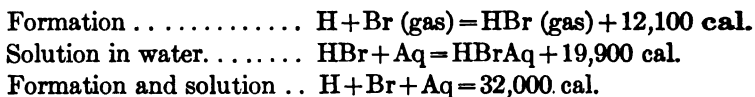
By *heat of formation* is meant the total heat produced when a compound is formed from its elements; as,

$$S + O_2 = SO_2 + 71,080 \text{ cal.}$$
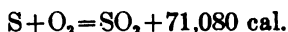
Heat of chemical union is similar to heat of formation, the uniting parts being compounds instead of elements; as,

$$CaO + CO_2 = CaCO_3 + 42,400 \text{ cal.}$$

Heat of decomposition is the opposite of heat of formation or of chemical union, or is equal in quantity but with opposite sign; as,

$$CaCO_3 = CaO + CO_2 - 42,400 \text{ cal.}$$
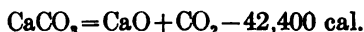
Heat of Solution.—By *heat of solution* is meant the total heat change produced when the substance is added until the water is saturated, or when water is added to the substance until there is no more heat change. The quantities of water and substance are taken in gram-molecular weights. We may roughly distinguish three cases: (1) There is simple solution without hydration or chemical action, and with or without ionization; (2) there is formed a definite hydrate with water; (3) there is chemical action. The investigations of Julius Thomsen, Berthelot, and others have established the following facts:

1. Anhydrous or dehydrated salts which do not form crystallizable hydrates and are not completely decomposed by water dissolve with absorption of heat. To this group belong the haloid compounds of potassium, lead, thallium, mercury, and silver, cadmium iodid, gold bromid, the potassium-haloid compounds of platinum, palladium, and mercury; most salts of potassium and many salts of lead, thallium, and silver.

2. Most anhydrous or dehydrated salts which form crystallizable compounds with water, or which are completely decomposed by water, dissolve with evolution of heat. To this group belong the halids generally, except those mentioned above, potassium carbonate, most of the salts of sodium, and the dehydrated salts of the magnesium group.

Sodium chlorid and sodium bromid belong to neither of these groups. They dissolve with absorption of heat.

3. Most hydrated salts dissolve in water with absorption of heat; a few dissolve with evolution of heat. Among the latter are the sulfates of lithium, glucinum, and manganese, and the chlorids of magnesium, manganese, iron, cadmium, and copper. Thomsen supposes that these salts exist in solution in a higher state of hydration.

Heat of Dilution.—By heat of dilution is meant the total heat produced when a given quantity of water is added to a solution of given strength. A solution of one gram-molecular weight of sodium sulfate in 50 molecules of water absorbs upon addition of 50 molecules more of water, 665 calories. The addition of 30 molecules of water to a solution of a mol. of magnesium sulfate in 20 mols. of water causes the development of 279 calories.

Heat of Hydration.—The heat of hydration is the quantity of heat produced during the combination of a mol. of the substance with the amount of water necessary to the production of a definite hydrate; as,

$$Na_3PO_4 + 10H_2O = Na_3PO_4,10H_2O + 23,520 \text{ cal.}$$

Heat of Chemical Solution.—When chemical combination takes place between the substance and water, the heat evolved will be partly due to solution, but mainly to the chemical action. Sulfuric oxid dissolves in water according to the following table:

(SO_3,H_2O). . . . . $= 21,320$ cal. $(SO_3,3H_2O)$. . . . . . $= 30,738$ cal.
$(SO_3,2H_2O)$. . . . . . . $= 27,699$ cal. $(SO_3,1600H_2O=)$. . $= 39,165$ cal.

It is seen that more than half the total heat is produced by the addition of the first molecule of water, and that the increase of heat for the third molecule is only half that for the second, and that but little more heat is evolved after the addition of the third molecule.

Heat Determinations.—The heat of reactions may be measured in various ways. The method most convenient is to observe the physical change which is produced in some standard substance; as, for example, the amount of ice which is melted at 0°, or the rise in temperature which is caused in a given quantity of water. The latter is the one most used.

There are various forms of calorimeters, only two of which need be mentioned here. The first is the common water-calorimeter used for substances in solution. It consists essentially of two vessels, an inner one, usually of platinum, into which the solutions are introduced, and an outer one containing a given quantity of water. The heat produced is measured by the rise in temperature in the solution itself and in the water surrounding the inner vessel. The thermometers used are graduated with great accuracy and various corrections are made for the temperature of the experiment, for the specific heats of the vessels and of the solutions, for changes of volume, etc.

The second form of apparatus is used in combustions. The substances are enclosed within a steel bulb, called an *explosion-bomb*, which is filled with oxygen under a pressure of 25 atmospheres. Substances which burn slowly in the air are rapidly consumed in compressed oxygen. The combustion is started by passing an electric current through an iron wire in contact with the mixture. The bulb is enclosed in a water-calorimeter and the heat is measured in the usual way.

Heat at Constant Volume and at Constant Pressure.—If there is no change in volume, no work is done, and the heat evolved represents the difference between the intrinsic energy of the substances reacting and that of those formed; that is, the whole of the energy of the reaction appears as heat. In most reactions involving only solids and liquids, the change of volume is so small that its effects may be neglected. If a gas is produced, there may be a great change of volume and consequently an appreciable amount of work. The heat appearing will, therefore, be less than the total energy of the reaction. This difference has been found to be $2T$ calories for each mol. of gas formed, T being absolute temperature. If a gas disappears, the heat will be increased by $2T$ calories for each molecule of gas condensed. For example, when hydrogen and oxygen combine in the bomb-calorimeter at

constant volume and at 18°, the heat produced is 67,487 calories. If the reaction took place at constant pressure, say in the atmosphere, water would be formed instead of steam, and 1 molecule of hydrogen and $\frac{1}{2}$ molecule of oxygen would disappear. The heat therefore would be increased by

$$1.5 \times 2 \times (273 + 18) = 873 \text{ calories,}$$

and the heat of union of hydrogen and oxygen at constant pressure is $67,487 + 873 = 68,360$ calories.

Laws of Thermochemistry.—The laws ot thermochemistry and the data upon which they are based have been carefully studied by Lavoisier, La Place, Hess, Favre, Silbermann, Berthelot, Julius Thomsen, Ostwald, and many others. · Especially notable has been the work of Pierre Eugene Berthelot of Paris and Julius Thomsen of Copenhagen. The most important laws of thermochemistry are as follows:

1. Law of molecular work. *The quantity of heat set free in a reaction is a measure of the total work, chemical and physical, done in the reaction.*

2. Law of heat of formation and decomposition. *The heat of decomposition of a substance is exactly equal to the heat of its formation.* This law was first announced by Lavoisier and La Place.

3. The law of initial and final state. *The quantity of heat generated by a chemical action is the same whether it takes place in one or several stages.* This law was discovered by G. H. Hess, a German chemist, in 1840.

4. The law of maximum work. *Every chemical change accomplished without the aid of outside energy tends to the production of that body or system of bodies, the formation of which sets free the maximum quantity of heat.*

To illustrate the law of maximum work, we may take the following reactions:

$$K + Cl = KCl + 105,680 \text{ cal.,} \quad K + Br = KBr + 95,380 \text{ cal.}$$

Chlorin should therefore replace bromin, and it does so as follows:

$$KBr + Cl = KCl + Br + 10,000 \text{ cal.}$$
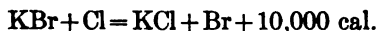
To the law of maximum work there seems to be many exceptions. There are endothermic reactions which take place spon-

taneously and there are exothermic compounds which cannot be directly formed. The heat of formation of I_2O_5, as found by Thomsen, is 40,030 calories, yet iodin and oxygen cannot be made to combine directly. It is possible that these exceptions will be explained and that the law will yet be found to be rigidly correct.

Indirect Heat Determinations.—The law of Hess is of the greatest importance in thermochemistry. The heat of formation can be determined in comparatively few cases. This law furnishes a simple means of indirect determination. For example, CO cannot be formed synthetically, but we have the following:

$$C + O_2 = CO_2 + 97,000 \text{ cal.}$$
$$CO + O = CO_2 + 68,000 \text{ cal.}$$
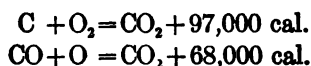
According to the law of Hess, the difference between these is the heat of formation of CO, and hence

$$C + O = CO + 29,000 \text{ cal.}$$
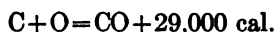
In a similar manner the heat of a reaction may be computed. It is equal to the difference between the heat of decomposition of the substances entering the reaction and the heat of formation of those emerging from it. The heat of the elements is zero. Since the heat of formation is equal to the heat of decomposition, we may substitute for the molecular formulas in an equation the heats of formation, and find the heat of the reaction by the following general equation:

$$A + B = C + D - x.$$

Examples.—
$$MgCl_2 + 2Na = 2NaCl + Mg - x.$$
$$151,000 + \quad 0 \; = 195,400 + \; 0 \; - x.$$
$$x = 239,800 \text{ cal.}$$
$$KHO \, Aq + HCl \, Aq = KCl \, Aq + H_2O \; - x.$$
$$116,460 \; + 39,315 \; = 101,340 \; + 68,360 - x.$$
$$x = 13,925 \text{ cal.}$$
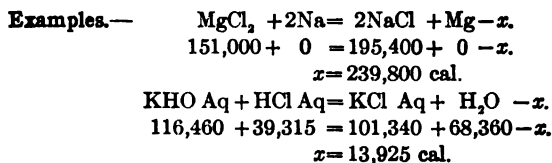
Any one of the heats of formation can be computed in the same way if the heat of the reaction and the heats of formation of the other compounds are known. By the last equation the heat of formation of KCl is found as follows:

$$116,460 + 39,315 = x + 68,360 - 13,925.$$
$$x = 101,340 \text{ calories.}$$

Heat of Combustion.—The *heat of combustion* is the heat produced when a substance is completely burned in oxygen. It is equal to the difference between the heat of formation of the compound burned and that of the products of the combustion. The heat of combustion is easily measured and is much used in the indirect determination of heats of formation. The heat of combustion of methane is as follows:

$$CH_4 + 4O = CO_2 + 2H_2O \quad -211,900 \text{ cal.}$$
$$x + 0 = 97,000 + 2 \times 68,300 - 211,900 \text{ cal.}$$
$$x = 21,700 \text{ cal., the heat of formation of methane.}$$
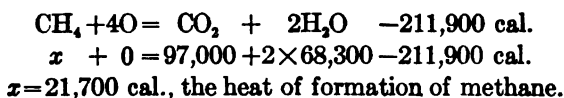
Thermoneutrality of Salt Solutions.—Salt solutions are highly dissociated, and if their ions do not react there is no heat change when they are mixed. This law of thermoneutrality of salt solutions was first observed by Hess. There is no heat production because there is no chemical action.

Heat of Neutralization.—By heat of neutralization is meant the heat which is evolved when equivalent quantities of an acid and a base are brought together in dilute solution. If the ions of two solutions unite to form undissociated compounds, the heat of their union will appear. If acid, base and salt are all dissociated, the only compound formed is water, and the heat of neutralization will be the heat of union of the ions $H \cdot$ and HO'. The heat of neutralization of strong acids and strong bases has been found to be constant and equal to 13,700 calories. For example:

$$H \cdot, Cl' \text{ Aq} + Na \cdot, HO' \text{ Aq} = Na \cdot, Cl' \text{ Aq} + H_2O + 13,700 \text{ cal.}$$
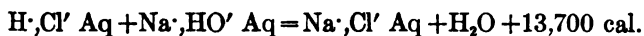
Or, since the sodium and chlorid ions remain unchanged, the real reaction is only between the ions,

$$H \cdot + HO' = H_2O + 13,700 \text{ cal.}$$
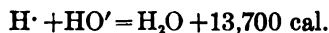
If the acid and base are weak, the dissociation will not be complete, and as fast as the ions are removed new ones will be supplied by further dissociation which will involve heat changes. Furthermore, an undissociated salt may be formed. These changes may increase or diminish the heat of neutralization. For example:

Formic acid and sodium hydroxid yield 13,400 calories.

Phosphoric acid and sodium hydroxid yield 14,830 calories.

Acetic acid and ammonium hydroxid yield 11,900 calories.

Basicity of Acids by Heat of Neutralization.—If a gram-molecular weight of an acid be dissolved in a large quantity of water and a base be added by molecular weights, the acid will be neutralized when no more heat is produced. The number of equivalents of the base required will indicate the basicity of the acid.

Examples.—

$$HCl + \tfrac{1}{2}NaOH = 6,000 \text{ calories.}$$
$$HCl + NaOH = 13,700 \text{ "}$$
$$HCl + 2NaOH = 13,700 \text{ "}$$
$$H_2SO_4 + NaOH = 14,500 \text{ "}$$
$$H_2SO_4 + 2NaOH = 31,000 \text{ "}$$
$$H_2SO_4 + 3NaOH = 31,000 \text{ "}$$

Hydrochloric acid requires one molecule of sodium hydroxid for its neutralization and is therefore monobasic; sulfuric acid requires two and is dibasic.

Heat of Formation of Allotropes and Isomers.—Several elements exist in two or more allotropic forms. When one of these forms is changed into another there is always heat change. This change is best measured indirectly by heat of combustion. $(P_2O_5) = 369,100$ calories when the phosphorus is in the ordinary form; $(P_2O_5) = 326,800$ calories when the phosphorus is amorphous. The difference is 42,300 calories; or in changing 62 grams of ordinary into amorphous phosphorus, 42,300 calories of heat are evolved.

So also isomeric compounds show different heats of formation and combustion. The heat of combustion of acetic acid, $C_4H_4O_2$, is 210,000 calories, while that of the isomeric methyl formate is 252,000 calories. This difference is due to the fact that the heat of decomposition of one molecule is greater than that of the other.

Calorific Intensity of Reactions.—The heat developed in chemical reactions is called *calorific power*. The maximum theoretical temperature to which the products are raised is called the *calorific intensity*. Calorific power is constant whether the action be slow or rapid. Calorific intensity depends upon the rapidity of the action and other attendant conditions. The theoretical temperature is never realized.

The calorific intensity is equal to the calorific power divided by the sum of the products of the weights and specific heats of the

products of the reaction.   If P represent the calorific power, I the calorific intensity, m, m', m'', etc., the weights, and s, s', s'', etc., the specific heats of the products, then

$$I = \frac{P}{ms + m's' + m''s'' + \ldots}$$

In this computation must be included the physical state of the products and the effects of any other substance which may be present, such as nitrogen of the air, ash, and unburned substances.

Example.—For a simple example we take the case of hydrogen burned in oxygen,

$$H_2 + O = H_2O + 68,924 \text{ cal.}$$

From this must be subtracted the heat of condensation of steam, 9,670 cal. The remainder is 59,254 cal.   The specific heat of steam is 0.475.   Making the substitutions, we have for the theoretical temperature

$$I = \frac{59,254}{18 \times 0.475} = 6930°.$$

Bunsen observed a temperature of 2844°.

For the union of CO with O we have $CO + O = CO_2 + 68,000$ cal. The molecular weight of CO_2 is 44, and its specific heat is 0.2164.   We have then

$$I = \frac{68,000}{44 \times 0.2164} = 7143°.$$

The temperature observed by Bunsen was 3003°.

Radiant Energy.—Energy transmitted through ether is called *radiant energy.* Its presence is made known through our senses only when it meets with ponderable matter and is transformed into those energies with which we are familiar. It is supposed to be due to ethereal vibrations, but so far as we know, there is no quantitative relationship between the ether and the energy, such as there is between matter and the usual forms of energy.

Radiant energy may be converted into any of the ordinary forms of energy, but generally appears as light and heat. It may produce mechanical motion as in the radiometer, and it is the agent which induces 'many important chemical actions. It is the chemical effects of radiant energy with which we are now specially concerned and the study of which is called *Photochemistry.*

The sun is the chief source of radiant energy. This energy comes to us mainly as heat and light, but investigation has shown that there are many rays which are not perceptible as heat and light, and these are in some cases the particular rays which produce the greatest chemical effect. Such are the ultra-red and the ultra-violet rays of the solar spectrum.

History of Photochemistry.—The action of light upon silver salts was first observed by Schultze in 1727. In 1777 Scheele photographed the spectrum and found that the chemical effect was not the same for light of different colors. In 1801 Ritter discovered that chemical action was produced by rays outside of the spectrum. Photography was discovered by Daguerre in 1838. Liebig in 1840 and J. R. Mayer in 1842 investigated the action of sunlight upon green plants. Later investigations were made by Draper (1862), Hankel (1862), Bunsen and Roscoe (1862), and others.

Chemical Action of Radiant Energy.—It has been shown that all light, including the ultra-red and the ultra-violet rays, may

produce chemical action. Silver salts are affected most by the ultra-violet rays, while it is the yellow light which is the chief agent in the manufacture of starch in the leaves of plants.

The applications of the chemical action of light in the arts are quite limited, photography and certain bleaching processes being the principal ones. In nature, however, this action is of the greatest importance. Practically all of the terrestrial energy available to man comes as radiant energy from the sun. The sun's heat is the general cause of meteorological phenomena. Wind and rain, storm and flood, summer heat and winter cold are dependent upon the sun's thermal rays. Sunlight, on the other hand, is the source of the potential chemical energy stored up in the bodies of plants and animals and in beds of coal and reservoirs of petroleum. It supplies the food of man and beast and furnishes the fuel which gives heat for our homes and power for our railroads and industrial plants. Through the help of light the protoplasm of the green leaf is able to decompose the carbon dioxid of the atmosphere and combine the carbon with water to make starch and other allied substances, and from these all plant tissues are built up.
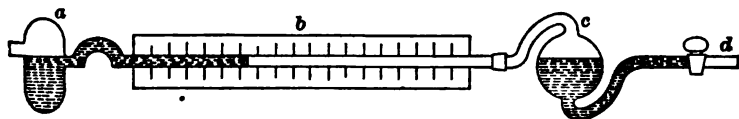
FIG. 44.—ACTINOMETER.

Actinometers.—The chemical activity of light is measured by *actinometers*, of which there are two classes, chemical and electric.

The *hydrogen-chlorin actinometer* used by Draper and improved by Bunsen and Roscoe is based upon the action of light upon a mixture of hydrogen and chlorin. The chamber c, Fig. 44, whose lower blackened half is filled with water, contains a mixture of equal volumes of hydrogen and chlorin obtained by the electrolysis of hydrochloric acid. The chamber a contains water and is connected with c by the tube b, which is furnished with a scale. When light is allowed to fall upon the upper portion of c, hydrogen chlorid is formed. This dissolves in the water, the volume of the gas is diminished, and the water from a moves along the tube b. The

reading on the scale is taken as a measure of the chemical activity of the light.

A more convenient apparatus is the *silver-chlorid actinometer*, in which the amount of chemical action is measured by the degree of blackening of paper covered with silver chlorid.

The *electric actinometer* measures the actinic intensity by the strength of the current induced by the action of light. Becquerel used two plates of silver coated with silver iodid, immersed in a solution of common salt and connected with a galvanometer. When light is allowed to fall on one of the plates, the silver iodid dissociates, the iodin ion goes into solution, the silver ion is deposited on the plate as metallic silver, and the plate becomes charged. The plate which has not been exposed to light gives off silver ions into the solution and becomes negatively charged. An electric current is thus produced whose electromotive force measured by the galvanometer indicates the amount of photochemical action.

Chemical Equivalent of Light.—Light disappears when it does chemical work, and it would seem possible to determine its chemical equivalent. Quantitative determinations of light are very difficult, however, and since rays of different wave-lengths produce widely different chemical effects, it is possible only to make rough approximations. Bunsen and Roscoe passed the light from a gas jet through a cylinder of chlorin and measured the loss; then through a cylinder twice as long filled with a mixture of equal volumes of hydrogen and chlorin, and found the loss to be much greater. The difference of loss, which was about one third of the radiation, represented the light which was converted into chemical energy.

Generally only a very small portion of the light which falls upon a sensitive substance is chemically active. Pfeffer estimated that 0.0000000537 gram of starch was formed in a square centimeter of the surface of an oleander leaf per second. The heat of combustion of so much starch is 0.00022 calorie. The total radiant energy received by a square centimeter on a summer day is about 0.03 calorie per second. The plant leaf, then, is able to use in the formation of starch less than one hundredth part of the light it receives.

Photochemical Laws.—John William Draper in 1842 proved that *photochemical action varies directly as the intensity of the light.*

He passed light through a lens and let it fall upon a hydrogen-chlorin actinometer. He then covered the lens with sectors of known angle and found that the action was proportional to the uncovered surface of the lens. The law was confirmed in 1862 by Hankel and by Bunsen and Roscoe.

Bunsen and Roscoe found also that with a light of given intensity *the action is proportional to the time of exposure.*

These two laws may be combined into one in the statement, *the photochemical action of light varies as the product of the intensity of the light and the time during which the light acts.*

Photolysis.—The decomposition or ionization of compounds by the action of light is called *photolysis* or *photolytic dissociation.*

Radioactivity.—There are radiations related to light but not visible which may be induced by electricity or may come from certain substances. These radiations penetrate bodies which are impervious to light, affect the photographic plate, render certain substances fluorescent, and present various other interesting phenomena. Some of them are of the nature of cathode rays, while others are supposed to be pulses or ripples in ether. In various forms they are known as *Röntgen rays, Becquerel rays,* and *alpha, beta,* and *gamma radium rays.*

Röntgen Rays.—William Conrad Röntgen of the University of Würtzburg in Bavaria, in 1895, while studying the cathode rays in a Crookes tube covered with black paper, observed that a sheet of paper covered with barium cyanplatinate lying near the tube became fluorescent. He inferred that rays similar to light rays coming from the tube through the black paper caused the fluorescence. On further investigation he found that these rays pass through wood, leather, paper, and so forth, but that metals were more or less opaque to them. They were called *X-rays* or *Röntgen rays.*

The Röntgen rays originate where the cathode rays strike a solid body like the walls of the glass tube or a plate of metal. Cathode rays are streams of very small negatively electrified particles flying with great velocity from the cathode in a vacuous tube. If they are focussed on a piece of metal by means of a concave cathode, the Röntgen rays proceed from the surface of the metal and pass out through the glass. If a fluorescent screen be held in the track of the rays and various objects be interposed, the trans-

parency of the objects to the rays will be made manifest. The rays were found to penetrate most bodies but with different degrees of ease. They passed readily through wood and leather, but were absorbed by heavy metals, except in very thin sheets. If a hand be interposed, a shadow of the bones is cast on the screen, because the rays pass readily through the flesh but are stopped by the bones. If the screen is replaced by a photographic plate, a picture is formed, called a *radiograph.* Röntgen rays ionize gases and are not refracted, reflected, nor polarized.

Becquerel Rays.—Henri Becquerel of Paris in 1896 discovered that compounds of uranium emit invisible rays which act on the photographic plate, pass through paper, wood, leather, and thin sheets of metal, ionize gases, and are not refracted, reflected, nor polarized. In 1898 G. C. Schmidt showed that thorium compounds act in much the same way. Such substances are said to be *radioactive* and the emanations are called *Becquerel rays.*

Radium Rays.—The investigations of M. and Mme. Curie of Paris, begun about 1898, led them to conclude that radioactivity is an atomic property. Some of the compounds of uranium and thorium were found to be more active than the elements themselves. This led them to hypothecate the existence of a new element of a much higher radioactivity. They were not able to isolate this element, which they called *radium,* but obtained compounds of it from which they were able to ascertain its properties and its atomic weight. Two other radioactive elements, polonium and actinium, are supposed to exist, but have not been separated. Radium possesses an intense radioactivity, more than 1,000,000 times greater than that of uranium.

The emanations from radium have been investigated by Becquerel, Ramsay, von Schweidler, Giesel, Villard, Rutherford, M. and Mme. Curie, and others. They have been found to be a mixture of several kinds of rays of which three kinds predominate and are characteristic. These are called by Rutherford *alpha-, beta-,* and *gamma-rays.*

1. The α-rays constitute the principal part of the emanation. They have not much penetrating power, and are slightly deflected by a magnetic field in a direction opposite that of the cathode rays. They seem to be streams of material particles or corpuscles charged with positive electricity.

2. The β-rays are more penetrating than the α-rays, and are strongly deflected in a magnetic field in a direction opposite to
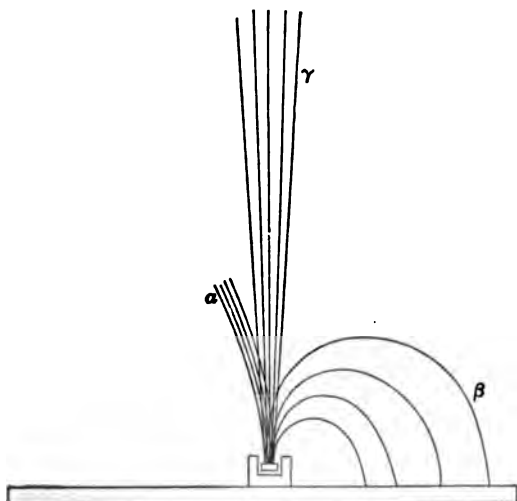
FIG. 45.—RADIUM RAYS.

that of the α-rays. They are streams of material particles charged with negative electricity, and are probably identical with the cathode rays. They are free electrons, the "corpuscles" of Thomsen, the "satellites" of Kelvin.

3. The γ-rays are very penetrating, are not affected by a magnetic field, and are not reflected, refracted, nor polarized. They seem to be identical with the Röntgen rays.

These rays all act on photographic plates, illuminate phosphorescent screens, and ionize gases.

The accompanying figure, taken from a paper published by Mme. Curie in the *Chemical News*, will serve to illustrate the radium rays. A bit of radium chlorid is placed in a cavity in a block of lead. A sheaf of rays shoots upward from the cavity. If a strong magnetic field be established near the receptacle, perpendicular to the plane of the paper and toward the back, the three kinds of rays will be separated. The heavy, positive α-rays will be slightly deflected to the left; the negative β-rays will be strongly deflected in circles to the right; and the penetrating γ-rays will pass directly

upward unchanged. If a photographic plate or a barium cyan-platinate screen is placed under the receptacle, the part will be affected where the β-rays fall. If the receptacle is covered with a thin sheet of aluminum, the α-rays are almost suppressed, the β-rays are lessened, and the γ-rays are scarcely diminished in intensity.

Theory of Radioactivity.—In 1903 Rutherford and Soddy proposed the theory of atomic disintegration as an explanation of radioactivity. In the same year Ramsay and Soddy actually obtained helium from radium bromid and identified it by its spectrum. According to the hypothesis of J. J. Thomson, the atom consists of numerous moving particles held together by their mutual forces. In complex atoms these particles may acquire such kinetic energy as to cause them to escape. The radium emanations are supposed to be of this character. The alpha emanations are positively charged particles twice as heavy as the hydrogen atoms, and are easily changed into helium. The beta emanations are negatively charged particles one thousandth the weight of the hydrogen atom. The escape of these particles is accompanied by the development of great energy. The quantities of material lost and energy evolved has been computed. Some of the estimates are as follows:

One gram of radium loses one half a milligram in alpha rays and less than one thousandth as much in beta rays in a year. It will lose half its weight in 1500 years. Uranium and thorium change about one millionth as fast.

One gram of radium gives out 100 calories of heat per hour. Its total heat emission is about 4×10^9 calories, which is a million times as great as that of any chemical action.

Electrons.—The term electron is applied to the beta particle. It is also used to represent the hypothetical atom of electricity, and the unit electric charge. Recent investigations have shown it to possess many curious properties, among which are the following:

1. It carries an electric charge of 3×10^{-10} electrostatic units.

2. Its linear dimension is about the one hundred thousandth that of an atom, the latter being the one ten millionth of a millimeter.

3. Its mean velocity is about one tenth that of light.

4. The electrons which are supposed to constitute the atom are comparatively far apart, their size and distance from one another being comparable to that of the planets in the solar system.

CHAPTER XIV.

ELECTROCHEMISTRY.

Electricity and Chemical Action.—Chemical action in the battery-cell gives rise to the electric current, and the electric current may be made to bring about an endless variety of chemical actions. A few years ago the center of interest was in the first transformation, since the battery was then the most important source of electricity. Now, since electricity can be produced in unlimited quantities by means of the dynamo, the application of electric energy to chemical operations on a large scale is attracting the attention of the world. Furthermore, the study of electrochemical phenomena has led to some of the most important discoveries of recent years, has brought about a new view of chemical actions, and has caused a revision of chemical theories. The study of electricity in its relationship to chemistry is called *electrochemistry*.

Conductors of Electricity.—There are two classes of conductors of electricity, conductors proper and electrolytes. In the first class the electric current produces no apparent change in the conductor except a rise of temperature. This change follows the *law of Joule*, which may be stated thus: *The quantity of heat produced by a current passing through a conductor is proportional to the square of the current if the resistance is constant, and to the resistance if the current is constant.* This law is empirical, but may be mathematically deduced. If electric energy, which is $cv = $ coulombs $\times$ volts, is changed into heat, h representing the heat in calories, we have $h = cv$. But $r = cr = $ current $\times$ resistance; and hence, $h = rc^2$.

Metals, alloys, carbon, and some other substances belong to the first class of conductors. There is the widest difference between the conductivities of different substances of this class. Metals are good conductors, while water, glass, wax, and rubber offer great resistance to the passage of the current. The ratio of the con-

157

ductivities of the best and poorest conductors is about 10^{20} **to 1.** It should be remembered that conductivity and resistance are reciprocals the one of the other.

Conductors of the second class are decomposed as the current passes through them, and hence the name *electrolyte,* from *electro* and *lutos,* a loosing.

Electrolysis.—Chemical decomposition effected by the electric current is called *electrolysis.* The action may be explained in the following way: The positive ions in contact with the negative electrode lose their charge to the electrode, neutralizing an equal amount of negative electricity and pass to the molecular state. So also the negative ions in contact with the positive electrode lose their charge and are separated in the molecular condition. The electric potential at the electrodes is thus lowered and the current is diminished by an amount equal to the charges given up by the ions. As the ions are removed they are replaced by further dissociation of the solute.

In the electrolysis of water and of acids hydrogen is set free at the cathode and oxygen at the anode. The acid radical or ion losing its charge at the anode acts upon the water present, taking the hydrogen to become the acid again and setting oxygen free. In the electrolysis of salts the metal goes to the cathode and the acid radical is disposed of as above. If the metal is one which can decompose water the hydroxid will be formed and hydrogen will be set free. In the electrolysis of bases the metal at the cathode acts upon water to restore the base, liberating hydrogen, and the hydroxyls at the anode form water and oxygen.

The Law of Faraday.—Investigations made in 1833 by Michael Faraday, an English physicist, led him to certain conclusions in regard to electrical action which are known as the *law of Faraday.* He made two generalizations which are of the greatest importance in electrochemistry. They may be stated as follows:

1. *The amount of decomposition effected in an electrolyte is proportional to the quantity of electricity which passes through it.*

2. *The amounts of different elements or ions separated by equal quantities of electricity are proportional to their ionic equivalents.*

The ionic equivalent is the weight of the ion divided by its valence. The current which separates 108 grams of silver will set free 35.45 grams of chlorin, 1 gram of hydrogen, 8 grams of

oxygen, 23 grams of sodium, 32.5 grams of zinc, 62 grams of NO_3, 48 grams of SO_4, etc.

Chemical Equivalent of Electricity.—All univalent ions carry the same amount of electricity. Bivalent ions carry twice as much, trivalent ions three times as much, and so on. In the electrolysis of a silver solution Lord Rayleigh and Mrs. Sidgwick found that one coulomb of electricity caused the deposition of 0.001118 gram of silver. The atomic weight of silver is 107.93, and therefore in order to separate a gram-atomic weight of silver there would be required $107.93 \div 0.001118 = 96,530$ coulombs of electricity. This amount of electricity is supposed to be carried by a gram-equivalent of each univalent ion. The *ionic electro-equivalent is therefore 96,530 coulombs.*

Electrolytic Dissociation or Ionization.—The partial decomposition of molecules into electrically charged ions is called *electrolytic dissociation* or *ionization.* As early as 1856, R. J. E. Clausius, a German physicist, in order to account for the fact that a very weak electric current will decompose even stable electrolytes, suggested the theory that the molecules of the solute are already broken down into ions under the influence of the solvent. In 1887 Svante Arrhenius, Professor in the University of Stockholm, revived this theory and started investigations which developed the present theory of electrolytic dissociation.

Heat, electricity, light, and the various forms of radiant energy are ionizing agents, but a much higher degree of dissociation is produced by the influence of a solvent upon a solute, water being most active in this regard.

Wilhelm Ostwald of Leipzig has shown that ions may be formed in four ways:

1. By molecular decomposition through an ionizing agent, as when acids, bases, and salts are dissolved in water, or when gases are subjected to radioactive influence:

$$HNO_3 = H^{\cdot} + NO_3{}' \qquad H_2SO_4 = H^{\cdot} + H^{\cdot} + SO_4{}'$$
$$KHO = K^{\cdot} + HO' \qquad Ca(HO)_2 = Ca'' + HO' + HO'$$
$$NaCl = Na^{\cdot} + Cl' \qquad Na_3PO_4 = Na^{\cdot} + Na^{\cdot} + Na^{\cdot} + PO_4'''$$
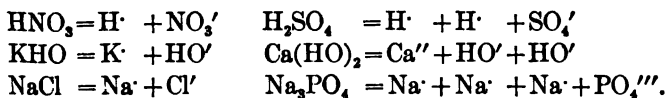
2. By molecular formation in the presence of an ionizing agent, as when chlorin water acts upon metals:

$$Au + Cl_3 = Au^{\cdots} + Cl' + Cl' + Cl'.$$
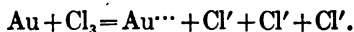
3. By transfer of electric charge, as when copper is displaced from solution by zinc:

$$Cu^{..}, SO_4'' + Zn = Zn^{..}, SO_4'' + Cu.$$
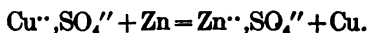
4. By increase or diminution of electric charge, that is, by change of valence, as in oxidation or reduction of compounds of metals:

$$Fe^{..} + Cl' + Cl' + Cl = Fe^{...} + Cl' + Cl' + Cl'.$$
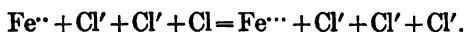
This equation is reversible, representing oxidation as it stands and reduction when reversed.

Mass Action and Ions.—Ostwald proved that ionization follows the law of mass action. When an acid, base, or salt is dissolved in water a portion of it ionizes and equilibrium is reached when the osmotic pressure of the ions is equal to the solution pressure of the substance. In a solution of common salt we have

$$NaCl = Na^{.} + Cl' \quad \text{and} \quad kp = k'p'q', \quad \text{or} \quad Kp = p'q',$$

in which p is the active mass of the undissociated sodium chlorid and p' and q' the active masses of the ions $Na^{.}$ and Cl'. K is called the *ionization constant* and depends upon the nature of the solute, the temperature, etc. Ostwald called it the *coefficient of affinity*, because in the case of acids the larger the constant the stronger the acid.

From this equation the following deductions may be made:

1. The larger the value of K the greater the dissociation. Practically it is found to be large for strong acids and strong bases and for most salts, while it is small for weak acids and weak bases.

2. If the value of K be increased by raising the temperature, p must diminish, and therefore the dissociation must increase. On the contrary, if the temperature is lowered, the dissociation is reduced.

The equation may be thrown into another form which for some purposes is more convenient. Let v equal the volume of the liquid which contains a mol of the solute, and a the percentage of dissociation; then $\dfrac{1-a}{v}$ is the amount undissociated and $\dfrac{a}{v}$ is

the amount of either ion, and the equation becomes

$$K\frac{1-a}{v}=\frac{a^2}{v^2} \quad \text{or} \quad K=\frac{a^2}{(1-a)v}.$$

From this expression for K it appears that as the volume of the solution increases the percentage of dissociation must increase, and that the dissociation is reduced when the volume is diminished. This is the *dilution law of Ostwald.*

This law holds good for weak acids and weak bases, but for reasons not explained good electrolytes do not follow it closely. Max Rudolphi suggested the substitution of $\sqrt{v}$ for v, and

$$K=\frac{a^2}{(1-a)\sqrt{v}},$$

which is called *Rudolphi's dilution formula,* gives results which are practically constant. Using ammonium chlorid he found the following:

v. ...	10	20	100	500	1000	5000
a....	0.852	0.887	0.940	0.971	0.979	0.991
K....	1.55	1.56	1.47	1.46	1.47	1.51

Van't Hoff proposed the dilution formula $K=\dfrac{a^{\frac{3}{2}}}{(1-a)\sqrt{v}},$ which gives values as nearly constant as those obtained from Rudolphi's formula.

The formula for the ionization constant is of great import in analytical chemistry. It gives a rational explanation of many peculiar actions. If to a solution ions be added which are like those present, the equilibrium will be disturbed, some of the ions will be driven back into combination, and the dissociation of the solute will be diminished. If, for example, hydrogen chlorid be added to a saturated solution of common salt, the excess of chlorin ions increases the product $p'q'$ and compels an increase in p, more molecular NaCl is formed, and, since the solution is saturated, it precipitates. So in many chemical reactions precipitation will be more complete when a substance is added which contains one of the ions which enters the precipitated substance. This principle finds wide application in both qualitative and quantitative analysis.

Ionization and Chemical Activity.—It is a fact that those conditions which are most favorable to ionization are the ones which best induce chemical action, viz., solution, fusion, vaporization, the presence of acid, base or salt, etc. It is also a fact that as a rule molecules are quite inactive. Phosphorus does not burn in dry oxygen, chlorin and sodium perfectly dry do not unite, dry hydrogen chlorid does not decompose carbonates nor unite with dry ammonia, and metallic sodium may be immersed in anhydrous sulfuric acid without action. In all these cases the presence of moisture induces vigorous action. A safe inference from these facts is that chemical action is mainly due to ions and that substances in the molecular condition resist chemical change.

Migration of Ions.—It has been shown that in electrolysis there is a movement of the ions, the positive towards the negative electrode and the negative towards the positive electrode. If a copper sulfate solution is electrolyzed between copper electrodes, copper is deposited at the cathode and dissolved at the anode. The color at the anode becomes deeper, showing an increase of concentration, while the color at the cathode fades, showing a diminution of concentration. There is a migration of the copper ions from the anode to the cathode, and in the same way the sulfate ion travels towards the anode. The change of concentration is explained by the theory of John Wilhelm Hittorf, a German physicist, on the supposition that different ions travel with different velocities. This will be understood from the accompanying diagrams, in which the plus signs represent positive ions and the minus signs negative ions:

$$\cdot \quad D$$

A. Cathode. $+ \; + \; + \; + \mid + \; + \; + \; +$ Anode.
                  $- \; - \; - \; - \mid - \; - \; - \; -$

B. Cathode. $+ \; + \; + \; + \; + \mid + \; + \; + \quad \_ \; \_$ Anode.
                $- \; - \; - \mid - \; - \; - \; - \; -$
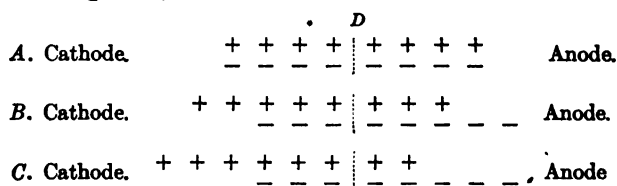
C. Cathode. $+ \; + \; + \; + \; + \; + \mid + \; + \quad \_ \; \_ \; \_$, Anode
              $- \; - \; - \mid - \; - \; - \; - \; -$

The electrolytic cell is divided by an imaginary porous partition into two compartments, the one containing the cathode and the other the anode. In *A* the concentration is uniform, four positive and four negative ions, or four molecules, being shown on each side of the partition *D*. If on passing a current of electricity the ions travel with equal velocities, the condition is shown

in B when two ions have passed the partition. The concentration still remains uniform though it has been reduced from four to three molecules in each compartment. If the ions travel with different velocities, say the positive twice as fast as the negative, we shall have, when three pairs of ions have been discharged, the condition in C. The concentration on the cathode side has been reduced from four to three, while that on the anode side has fallen from four to two. The loss of concentration is seen to be proportional to the velocity of the ion leaving the compartment; that is,

$$\frac{\text{Loss at anode}}{\text{Loss at cathode}} = \frac{\text{Velocity of cation}}{\text{Velocity of anion}} = \frac{u}{v}.$$

Relative Velocities of Ions.—The above equation enables us to determine the relative velocities of the ions when the original concentration is known and the loss at the anode and cathode for a given current has been determined. The investigations of Hittorf and others seem to establish the following laws:

1. The relative velocities of the ions are independent of the current strength.

2. The migration velocity of the cation sometimes increases and sometimes diminishes with the dilution until a certain dilution is reached, when it remains constant.

3. Between 4° and 20° the effect of change of temperature is small; but Löb and Nernst have shown that as the temperature rises the relative velocities of all ions approach the same value, 0.5.

Conductivity of Solutions.—The electric current is conveyed in solutions by the migrating ions. If both ions move, they share the transport; if only one moves, it carries the whole of the electricity. If one moves faster than the other, it carries electricity in proportion to its velocity. If u and v are the velocities of the cation and anion respectively, $\frac{u}{u+v}$ is the part of the current carried by the former, and $\frac{v}{u+v}$ is the part carried by the latter. These are the *transport numbers* of Hittorf. In an example given by Walker, the current which deposited 32.2 milligrams of silver in the silver voltameter was passed through the electrolytic cell and caused a fall of concentration at the cathode which corresponded to 16.8

milligrams of silver. The rise at the anode was the same, because the total silver nitrate in the solution remained unchanged. Had no silver ions migrated from the anode, the rise would have been 32.2, and hence the fall due to migration of the cations was $32.2 - 16.8 = 15.4$. We have then for the relative velocities

$$\frac{u}{v} = \frac{15.4}{16.8} = 0.917,$$

and for the transport numbers

$$\frac{u}{u+v} = \frac{15.4}{32.2} = 0.478 \quad \text{and} \quad \frac{v}{u+v} = \frac{16.8}{32.2} = 0.522.$$

Specific Conductivity.—The conductivity of a solution must be stated with reference to some standard form. The form most convenient is a cube of the solution at 0° with an edge equal to 1 centimeter. The resistance of such a cube in ohms is called the *specific resistance*, and the reciprocal of this is the *specific conductivity*.

Another form used is a cylinder of the solution 1 meter long and 1 square millimeter or 0.01 square centimeter in cross-section, as compared with a similar column of mercury at 0°. This is called the *Siemens unit*, and is converted into ohms by dividing it by 1.063. Since conductivity is proportional directly to cross-section and inversely to length, the first unit is 10,000 times as large as the second:

$$\frac{0.01}{100} : \frac{1}{1} :: 1 : x. \quad x = 10,000.$$

Molecular Conductivity.—Since water is practically a non-conductor, the conductivity of a solution will depend upon the electrolyte. In order that the conductivities of different solutions may be compared, it is necessary to use comparable quantities of the solute. The quantity most convenient is the gram-molecular weight or the gram-equivalent weight. The conductivity of a solution containing a mol of the solute and placed between electrodes 1 centimeter apart and large enough to contain between them the whole of the solution is called the *molecular conductivity*. Since the specific conductivity is taken with reference to 1 cc. the molecular conductivity will be equal to the specific conductivity

multiplied by the volume of the solution in cubic centimeters.   If *m* equals the molecular conductivity, *v* the volume in cubic centimeters, and *s* the specific conductivity, then

$$m = vs.$$

In a normal solution, which contains 1 mol to 1000 cc., $m = 1000\ s$. If *s* is the specific conductivity, taken with reference to a column 1 meter in length and 1 square millimeter in section, then $m = 10,000\ vs$.

The *equivalent conductivity* is that referred to a solution containing 1 equivalent instead of 1 mol.

Conductivity Measurements.—Conductivity measurements are best made according to a method devised by Friedrich Kohlrausch,

Fɪɢ. 46.—Cᴏɴᴅᴜᴄᴛɪᴠɪᴛʏ Mᴇᴀsᴜʀᴇᴍᴇɴᴛ.
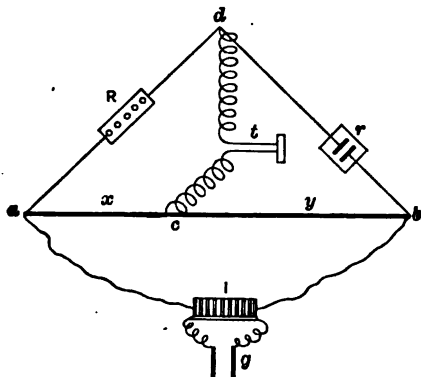
a German physicist, which is illustrated in the accompanying diagram.   The solution is placed in the electrolytic cell *r* with electrodes of platinum covered with platinum black.   *R* is a rheostat or Wheatstone bridge for measuring resistance, *g* is a battery connected with a small coil *i* which furnishes an alternating current, *ab* is a meter measure along which lies a wire of platinum or manganine (alloy of German silver and manganese), *t* is a telephone receiver connected with the circuit at *d* between the rheostat and the electrolytic cell and with the platinum wire by a sliding contact *c*.   The current passes through the wire *ab*, and through the rheostat *R* and the electrolyte *r* in the circuit *adb*, and also through

the telephone circuit *dtc*, causing the hum of the induction coil to be heard in the telephone. When on moving the slide *c* the distance *ac* is to the distance *cb* as the resistance at *R* is to the resistance at *r*, no current passes through *dc* and the telephone becomes silent. We then have, if *ac=x*, *cb=y*, *R*=the resistance in the rheostat, and *r*=the resistance in the cell,

$$rx = Ry \quad \text{and} \quad r = \frac{Ry}{x}.$$

But the conductivity *c* is the reciprocal of the resistance and

$$c = \frac{x}{Ry}.$$

This would be the specific resistance if the electrodes had an area of 1 square centimeter and were 1 centimeter apart. If they were not so arranged, a constant *K* must be determined for the cell and the value becomes

$$c = \frac{Kx}{Ry}.$$

For molecular conductivity we have, *v* being the volume in cubic centimeters which contains one mol of the solute,

$$c_m = \frac{Kvx}{Ry}.$$

Conductivity and Dilution.—It has been found that the conductivity of a solution increases with dilution up to a certain limit, when it becomes constant. This limit is rather improperly called *infinite dilution*, a term which simply means that dilution which gives the *maximum molecular conductivity*. This is illustrated by the following table, in which is given the molecular conductivity of hydrochloric acid for various volumes containing 1 mol of HCl:

Vol. in liters	1	10	100	1000	10,000
Mol. conductivity	278	324.4	341.6	345.5	345.5

The molecular conductivity becomes a maximum in good conductors at a dilution of from 1000 to 10,000 liters.

The maximum molecular conductivity can be measured in strong acid and strong bases and in salts, but in weak acids and in weak bases the dilution required for complete dissociation is so great that the direct determination is not practicable. It can, however, be indirectly estimated by applying the law of Kohlrausch (see next paragraph). A salt of the acid is formed and its maximum molecular conductivity determined. From this is subtracted the known constant for the metal; the remainder is the constant for the acid ion. To this is added the constant for the hydrogen ion and the sum will be the constant for the acid. For example, the dissociation of formic acid at 25° in a solution one thousandth normal is only 35 per cent, but its sodium salt is completely dissociated at moderate dilution. The maximum molecular conductivity of sodium formate at 25° is 99.2. Ostwald found the constant for sodium to be 49.2 and that for hydrogen to be 325. The constant for formic acid will therefore be $99.2 - 49.2 + 325 = 375$.

Independent Migration of Ions.—*Law of Kohlrausch.*—Kohlrausch observed that the difference between the molecular conductivities of two electrolytes having a common anion and different cations is the same as the difference between the molecular conductivities of two other electrolytes having another common anion and the same cations as before:

$$m_\infty \text{KCl} \quad - m_\infty \text{NaCl} \quad = 140 - 120 = 20.$$
$$m_\infty \text{KNO}_3 - m_\infty \text{NaNO}_3 = 135.7 - 113.7 = 22.$$

The same is true for common cations:

$$m_\infty \text{KBr} \quad - m_\infty \text{KNO}_3 \quad = 141 - 121 = 20.$$
$$m_\infty \text{NaBr} - m_\infty \text{NaNO}_3 = 120 - \quad 98 = 22.$$

The difference between these numbers does not exceed the experimental errors. m_∞ is the molecular conductivity at infinite dilution.

From these facts Kohlrausch arrived at the conclusion that *the molecular conductivity is the sum of two constants, the one dependent upon the anion and the other upon the cation.* Since conductivity is measured by the velocities of the ions, these constants will be proportional to these velocities and

$$m_\infty = u + v,$$

u depending upon the cation and v upon the anion. Therefore *the velocity of any ion as well as its conductivity is independent of other ions present with it in the solution.* This is the *law of Kohlrausch* or the *law of independent migration of ions.*

Ostwald has shown that the law holds good for any dilution provided we take into consideration the degree of dissociation. If a represents the percentage of dissociation, the equation becómes

$$m_v = a(u+v).$$

As the dissociation increases, the value of a approaches unity, which it becomes at infinite dilution.

Actual Velocity of Ions.—The actual velocity of ions may be determined experimentally. For this purpose Sir Oliver Joseph Lodge, an English physicist, used a long tube which contained the electrolyte along with an indicator. The rate at which the color in the indicator travels along the tube, corrected for diffusion of the liquids, is the rate of movement of the ions. With a difference of potential of 1 volt per centimeter, Lodge found the velocity of the hydrogen ion to be 0.0026 centimeter a second, or 1 centimeter in about six and a half hours.

The surprisingly slow movement of the ions through water is no doubt due to the enormous resistance with which they meet on account of friction. It has been calculated that the force required to drive 1 gram of hydrogen ions through water at the rate of 1 centimeter a second is equal to 300,000 tons weight.

The actual velocities of the ions may be computed as follows: The conductivity or sum of the velocities $u+v$ is found at infinite dilution, and the relative velocities $\dfrac{u}{v}$ are obtained by Hittorf's method, then by a simple algebraic process the values of u and v are found.

The velocities of a number of ions as determined by Kohlrausch are as follows:

Cations.	Cm. per second.	Anions.	Cm. per second.
Hydrogen	0.00320	Hydroxyl	0.00182
Potassium	0.00066	Chlorin	0.00069
Sodium	0.00045	Iodin	0.00069
Ammonium	0.00066	NO_3	0.00064
Silver	0.00057	ClO_3	0.00057

Conductivity and Dissociation.—Since in electrolytes the current is conducted through the ions, the conductivity will be zero when there is no dissociation. If the dissociation is complete the conductivity will reach a maximum. Conductivity, therefore, varies with the dissociation and becomes a means of measuring it. The percentage of dissociation is obtained by dividing the molecular conductivity for any given dilution by the maximum conductivity, or the conductivity at infinite dilution. If d is the dissociation we have

$$d = \frac{m_v}{m_\infty}.$$

The following table gives the percentage of dissociation of a few substances in normal, decinormal, centinormal, and millinormal solutions:

Liters.	HCl	NaCl	H_2SO_4	KHO	NH_4OH
1	81	70	45	80	2
10	94	84	60	93	5
100	99	94	80	99	13
1000	100	98	97	100	20

Dissociating Power of Solvents.—Water is the most powerful dissociant known. The study of other liquids is difficult because of the great dilution required for complete dissociation in them. Much work, however, has been done along this line. The following liquids have a dissociating power about in the order in which they are mentioned: Formic acid (three fourths that of water), nitric acid and methyl alcohol (two thirds that of water), ethyl alcohol (one third that of water), ammonia (one fourth that of water), sulfurous oxid, acetone, etc.

Ionization of Fused Substances.—Many substances become conductors as the temperature rises, and at the melting-point possess such conductivity as to indicate that they are quite highly ionized. Such substances undergo electrolysis, and many metals may be prepared in this way.

Electrolytic Solution Tension.—The idea of electrolytic solution tension is due to Walther Nernst. When a metal is immersed in water, some of its atoms will pass into solution as positive ions, taking their electric charge from the metal and thus rendering it negative. The attraction between the positively charged ions and the negatively charged metal causes the formation at

the surface of the metal of the so-called double layer of Helmholtz, and a difference of potential arises. The tendency of the metal to go into solution is called its *electrolytic solution tension,* and equilibrium is established when this tension is equal to the osmotic pressure of the ions.

When a metal is immersed in a solution of one of its salts, the same thing occurs, but since the solution already contains the ions of the metal, fewer ions will be separated and equilibrium will sooner be reached. If a positive charge is given to the metal, more ions will go into solution. It is upon this principle that electroplating is effected. If the positive electrode is copper, the current forces copper ions into solution, and these, coming into contact with the negative electrode, are relieved of their charge and deposited as copper.

The electrolytic solution tension has been determined for the principal metals and has been found to exhibit enormous differences in value. Such metals as magnesium, zinc, aluminum, cadmium, iron, and cobalt are negative when in contact with solutions of their salts. This means that their solution tension is greater than the osmotic pressure of the metal ions in the solution. Gold, copper, silver, mercury, and lead are positive in solutions of their salts; that is, their solution tension is less than the osmotic pressure of the metal ions. In the following table is given the electrolytic solution tensions of various metals in normal solutions of their salts, the value of the osmotic pressure of the metal ions being taken as 22 atmospheres.

Metal.	Atmospheres.	Metal.	Atmospheres.
Magnesium............	10^{44}	Nickel................	10^{0}
Zinc.................	10^{18}	Lead.................	10^{-2}
Aluminum...........	10^{13}	Mercury..............	10^{-16}
Cadmium............	3×10^{6}	Silver................	10^{-17}
Iron................	10^{4}	Copper...............	10^{-20}
Cobalt...............	2×10		

This is called the *electrolytic tension series* of metals. Each metal will have a tendency to displace from solution any one below it in the series. The precipitation of gold, silver, and copper from their solution by zinc is a familiar action.

CHAPTER XV.

CHEMICAL CALCULATIONS.

Basis of Calculations.—Since symbols and formulas represent definite quantities, since reactions take place between definite masses and volumes, and since equations represent these reactions, it follows that symbols, formulas, and equations furnish the data for all sorts of chemical calculations. These usually involve only simple arithmetical operations and are of two kinds, those based upon weight or mass and those based upon volume.

WEIGHT CALCULATIONS.

Atomic Weight.—The atomic weight is indicated by the symbol and is to be taken from the table of atomic weights. When atoms are multiplied, the atomic weight is multiplied. $O = 16$, $O_2 = 2 \times 16 = 32$.

Molecular Weight.—The molecular weight is found from the molecular formula by adding together the atomic weights. Care must be taken to include all the atoms found in the formula.

$$SO_3 = 32 + 3 \times 16 = 80. \quad Ca(NO_3)_2 = 40 + 2(14 + 3 \times 16) = 164.$$

The molecular weight is twice the density, and the molecular formula must always represent this amount.

Quantity of an Element or Group.—Each element composes such a part of any mass as its atomic weight is part of the molecular weight. The molecular weight of PbO is 223. Of this 207 is lead, or $\frac{207}{223}$ of the whole. One hundred kilograms of lead oxid contains $\frac{207}{223} \times 100 = 82.82$ kilograms of lead.

A group is computed in the same way. The molecular weight of $CaCO_3$ is 100, that of CaO is 56. Ten grams of limestone will then yield $\frac{56}{100} \times 10 = 5.6$ grams of lime.

Exercise.—1. How much silver in 20 grams of $AgNO_3$?

2. How much iron in 100 kilograms of Fe_2O_3?

3. How much NH_3 can be obtained from 50 grams NH_4Cl?

Percentage Composition.—The relative amounts of the elements in the molecule are usually given as per cent. The computation is easily made as follows: The molecular weight of CO_2 is 44; of this 12 is carbon and 32 oxygen. Therefore $\frac{12}{44}$ of any amount of CO_2 is C, and $\frac{32}{44}$ is O. This is made per cent by multiplying by 100 and performing the division:

$$C = \tfrac{12}{44} \times 100 = 27.27\%. \quad O = \tfrac{32}{44} \times 100 = 72.73\%.$$

Per cent is always carried to the second decimal place, and the sum of the per cents must equal 100.

Exercise.—Find the percentage composition of (1) H_2SO_4, (2) $Ba(NO_3)_2$, (3) $Ca_3(PO_4)_2$. (4) Find the per cent of CO_2 in $NaHCO_3$, (5) NH_3 in NH_4Cl.

Formula.—To be able to write a molecular formula we must know how many atoms of each element are present. Having the molecular weight and the percentage composition, the number of atoms of each kind is found as follows: Divide each per cent by the atomic weight of the element and multiply the quotient by one per cent of the molecular weight. The molecular weight of a compound of C and O is 44, and it contains of C 27.27 per cent and of O 72.73 per cent.

For C, $\dfrac{27.27}{12} \times 0.44 = 1$ atom. For O, $\dfrac{72.73}{16} \times 0.44 = 2$ atoms.

The formula then is CO_2.

Demonstration.—Let a = atomic weight, n = the number of atoms, m = the molecular weight, and p = the per cent; then

$$p = \frac{100an}{m}. \quad \therefore n = \frac{p}{a} \times \frac{m}{100}.$$

Exercise.—Find the formulas of the following:

1. Ca = 29.41%, S = 23 53%, O = 47.06%, molecular weight = 136.
2. C = 85.71%, H = 14.29%, molecular weight = 28.
3. Si = 35.90%, H = 2.56%, O = 61.54%, molecular weight = 78.

Equations.—If an equation be written by molecular weights, the numbers represent the relative amounts of substances entering

into and coming out of the reaction.   The following equation:

$$HNO_3 + NaHO = NaNO_3 + H_2O$$
$$63 \; + \; 40 \; = \; 85 \; + \; 18$$
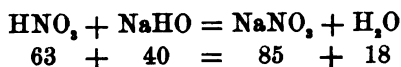
shows that 63 parts of HNO_3 act with 40 parts of NaHO to form 85 parts of $NaNO_3$ and 18 parts of H_2O.   Any quantity of one being given, the corresponding quantities of the others may be found by proportion.   Suppose 10 grams of HNO_3 are used, how much NaHO is required and how much $NaNO_3$ and H_2O is produced?

$$63 : 40 :: 10 : x; \quad x = \frac{40 \times 10}{63} = \; 6.35 \text{ grams NaHO.}$$

$$63 : 85 :: 10 : x; \quad x = \frac{85 \times 10}{63} = 13.49 \text{ grams NaNO}_3.$$

$$63 : 18 :: 10 : x; \quad x = \frac{18 \times 10}{63} = \; 2.86 \text{ grams H}_2O.$$

How much HNO_3 and NaHO is required to make 10 grams of water ?

$$63 : 18 :: x : 10; \quad x = \frac{63 \times 10}{18} = 35.00 \text{ grams HNO}_3.$$

$$40 : 18 :: x : 10; \quad x = \frac{40 \times 10}{18} = 22.22 \text{ grams NaHO.}$$

By inspection of these results we may discover the simple rule:

Multiply the given quantity by the molecular weight of the other substance and divide the product by the molecular weight of the given substance.

Exercise.—Equation $Zn + H_2SO_4 = ZnSO_4 + H_2$.
100 grams zinc require how much H_2SO_4 ?
20 grams zinc make how much $ZnSO_4$?
50 grams zinc make how much hydrogen ?
How much zinc required to make 10 grams hydrogen ?
How much $ZnSO_4$ is made in the production of 2 grams of hydrogen ?

VOLUME CALCULATIONS.

Hydrogen Unit.—The weight of a liter of hydrogen at 0° and 760 mm. is 0.08995 gram.   One gram of hydrogen then occupies 11.12 liters, and a gram molecules is 22.24 liters.   Since gaseous molecules are all of the same size, this number also represents the

volume of the gram-molecular weight of all gases. Thirty-two grams of O, 44 grams of CO_2, 17 grams of NH_3, etc., each occupy a volume of 22.24 liters.

Air is 14.38 times as heavy as hydrogen. The specific gravity of hydrogen is therefore $\dfrac{1}{14.38}$, or 0.0696.

Specific Gravity of Gases.—The specific gravity of any gas is obtained by multiplying its density by the specific gravity of hydrogen, 0.0696. For example, the molecular weight of CO_2 is 44, its density is 22, then its specific gravity is $22 \times 0.0696 = 1.53$.

Exercise.—Find the specific gravity of (1) SO_2, (2) NH_3, (3) CH_4.

To Find the Weight of One Liter.—To find the weight of a liter of any gas, multiply its density by the weight of a liter of hydrogen, 0.0899 gram. Example: the molecular weight of SO_2 is 64, its density is 32, and therefore one liter weighs $32 \times 0.0899 = 2.877$ grams.

Exercise.—Find the weight of a liter (1) of N_2O, (2) of Cl_2O_3, (3) of H_4Si, (4) of PH_4Cl.

To Find the Weight of a Given Volume.—To find the weight of a given volume of gas, multiply the volume in liters by the weight of a liter found as above.

Exercise.—Find the weight (1) of 10 liters of PH_3, (2) of 200 cc. N_2O_4, (3) of 500 cc. N.

To Find the Volume of a Given Weight.—To find the volume corresponding to a given weight of gas, divide the weight by the weight of one liter; the result will be the volume in liters.

Exercise.—Find the volume (1) of 20 grams nitrogen, (2) of 2 grams PCl_3, (3) of 5 grams C_2H_6.

Reduction for Pressure.—Volume of gases varies inversely as the pressure, that is, as the pressure increases the volume diminishes and *vice versa*. If v and v' be the volumes and p and p' the pressures, $v : v' :: p' : p$, or $v = \dfrac{v'p'}{p}$. This may be put into a rule thus: *Multiply the given volume by the given pressure and divide by the required pressure; the result will be the required volume.*

An easy method is this: *Make a fraction of the two pressures, considering whether the volume is to be increased or diminished, and multiply it by the given volume.*

Example.—100 cc. of hydrogen were measured at 750 mm.; what is the volume at 760 mm.? The pressure is increased, therefore the volume will be diminished, and hence $100 \times \dfrac{750}{760} = 98.8$ cc.

Exercise.—If 100 cc. of a gas are measured at 740 mm., what is the volume at 640 mm. ? Measured at 760 mm., volume at 720 mm.? Measured at 620 mm., volume at 760 mm.?

Reduction for Temperature.—Gaseous volumes vary directly as the absolute temperatures. If v and v' are the volumes and t and t' the absolute temperatures, then $v : v' :: t : t'$, or $v = \dfrac{v't}{t'}$. This means, multiply the given volume by the required temperature and divide the product by the given temperature. A very simple rule is as follows:

Reduce to absolute temperature by adding to the given and required temperatures each 273 degrees, then make a fraction of the temperatures, considering whether the volume is to be increased or diminished, and multiply the given volume by this fraction; the result will be the required volume.

Example.—If 100 cc. of a gas are measured at 17°, what is the volume at 0°? The corresponding absolute temperatures are $17 + 273 = 290°$ and $0° + 273° = 273°$. Since the temperature is to be lowered, the volume will be diminished and we will have $100 \times \dfrac{273}{290} = 94.14$ cc., the required volume.

Exercise.—1. 200 cc. are measured at 100°; what is the volume at 60°?
2. 1000 cc. are measured at 100°; what is the volume at 0° ?

Reductions for pressure and temperature may be combined in one operation, and by the use of logarithms the process is very much shortened.

Example.—165 cc. of a gas is measured at 27° and 740 mm.; what is the standard volume? The reduction is to 0° and 760 mm. The volume is diminished by the change of both temperature and pressure, and we have $165 \times \dfrac{273}{300} \times \dfrac{740}{760} = 146.2$ cc.

If the gas is measured over water, the barometer reading is diminished by the aqueous vapor tension for the given temperature. Thus, in the above example, the vapor tension at 27° is 26.5 mm., and the true pressure on the gas is $740 - 26.4 = 713.5$, and we have $165 \times \dfrac{713.5}{760} = 140.6$ cc.

The following table gives the vapor tension of water in millimeters of mercury for all temperatures that are likely to be used :

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
0°	4.6 mm.	12°	10.5 mm.	20°	17.4 mm.	29°	29.8 mm.
5°	6.5 "	13°	11.2 "	21°	18.5 "	30°	31.5 "
6°	7.0 "	14°	11.9 "	22°	19.7 "	31°	33.4 "
7°	7.5 "	15°	12.7 "	23°	20.9 "	32°	35.4 "
8°	8.0 "	16°	13.5 "	24°	22.2 "	33°	37.4 "
9°	8.6 "	17°	14.4 "	25°	23.6 "	34°	39.6 "
10°	9.2 "	18°	15.4 "	26°	25.1 "	50°	92.0 "
11°	9.8 "	19°	16.3 "	27°	26.5 "	100°	760.0 "

Exercise.—1. 200 cc. of a gas are measured at 33° and 475 mm.; what is the standard volume ?

2. 300 cc. of a gas are measured at 37° and 2 atmospheres; what is the standard volume ?

3. 500 cc. are measured at standard conditions; what is the volume — 140° and 10 atmospheres ?

Volume Equations.—The calculations based upon volume equations are very simple. They will be understood from an example. Alcohol burns according to the following equation:

$$C_2H_6O \quad + \quad 3O_2 \quad = \quad 2CO_2 \quad + \quad 3H_2O$$
$$\text{2 vols.} \quad + \quad \text{6 vols.} \quad = \quad \text{4 vols.} \quad + \quad \text{6 vols.}$$
$$\text{1 vol.} \quad + \quad \text{3 vols.} \quad = \quad \text{2 vols.} \quad + \quad \text{3 vols.}$$
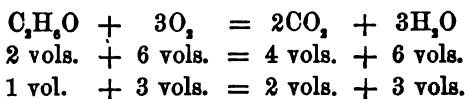
This means that to burn one liter of alcohol vapor 3 liters of oxygen are required, and that there are produced 2 liters of carbon dioxid and 3 liters of steam.

PART IV.

DESCRIPTIVE CHEMISTRY.

CHAPTER XVI.

THE ELEMENTS.

OF the seventy-seven or more elements which compose the innumerable substances of the earth only a few are of considerable abundance. Indeed two, oxygen and silicon, comprise three fourths of the solid crust of the globe. Six others, aluminum, iron, calcium, magnesium, sodium, and potassium, include twenty-four per cent of the remainder, leaving but one per cent for the other sixty-nine elements. Further, ten more elements constitute ninety-nine one-hundredths of this one per cent, so that only one one-hundredth of one per cent is left for the remaining fifty-nine. The following table, prepared by Professor F. W. Clarke, gives the estimated composition of the earth's crust, including the sea and atmosphere :

Oxygen	49.98 per cent.	Titanium	0.30 per cent.
Silicon	25.30 "	Carbon	0.21 "
Aluminum	7.26 "	Chlorin	0.15 "
Iron	5.08 "	Phosphorus	0.09 "
Calcium	3.51 "	Manganese	0.07 "
Magnesium	2.50 "	Sulfur	0.04 "
Sodium	2.28 "	Barium	0.03 "
Potassium	2.22 "	Nitrogen	0.02 "
Hydrogen	0.94 "	Chromium	0.01 "
		Total	99.99 "

Of these eighteen elements four are gases, ten are non-metals, and eight are metals, as follows:

Gases: hydrogen; nitrogen, oxygen, and chlorin.

Non-metals: chlorin, sulfur, chromium, phosphorus, carbon, silicon, titan'um, hydrogen, nitrogen, and oxygen.

Metals: sodium, potassium, magnesium, calcium, barium, aluminum, iron, manganese.

A brief description of these elements and of a few others is here given in order that the student may become at once familiar with them.

Hydrogen, atomic weight 1.—A colorless combustible gas, the lightest substance known, does not occur free in nature, liquefies with great difficulty, boiling-point −246°. Its principal compounds are water and organic substances.

Oxygen, atomic weight 16.—Colorless gas, supporter of life and combustion, the most abundant element, free in the air, liquefies under pressure and cold, boiling-point −182°. One fifth of the air and one half of the crust of the earth are oxygen. Its compounds are very numerous; it is a constituent of nearly every common object. Water and all the common rocks are examples.

Nitrogen, atomic weight 14.—Colorless gas, very inactive, free in the air, liquefied by cold and pressure, boiling-point − 194°. It has numerous familiar compounds; as, ammonia, nitric acid, niter, and ammonium chlorid. It is a constituent of plant and animal bodies and of most explosives.

Chlorin, atomic weight 35.4.—A heavy gas of greenish color, very poisonous and active, does not occur free. It forms many compounds of which hydrochloric acid, common salt, and potassium chlorid are examples.

Sulfur, atomic weight 32.—A brittle, yellow solid, easily melted, burns with stifling odor, insoluble in water, occurs free and combined. Of its numerous compounds the most important are sulfuric acid, the sulfates, and the native sulfids of the metals.

Phosphorus, atomic weight 31.—A soft, pale yellow solid, poisonous and very active, does not occur free, melts easily and burns at a low temperature. Its principal compounds are phosphoric acid and the phosphates.

Carbon, atomic weight 12.—Three forms: diamond, graphite, and charcoal. Diamond, transparent crystals, the hardest substance,

brilliant and costly. Graphite, soft, black, somewhat abundant, used for making lead-pencils. Charcoal, soft, porous, made by charring wood. Principal compounds, carbon dioxid, carbonates, and organic bodies.

Silicon, atomic weight 28.—Steel-gray solid, does not occur free, next in abundance to oxygen. Familiar compounds, quartz and the hard rocks generally.

Titanium, atomic weight 48.—A gray solid, difficult to separate from its compounds, a constituent of some rocks and associated with iron ores.

Sodium, atomic weight 23.—Silver-white, soft, very active, tarnishes in the air, decomposes water, strongly alkaline. Most familiar compounds, common salt and cooking-soda.

Potassium, atomic weight 39.—Soft, bluish solid, very active, decomposes water, tarnishes instantly, does not occur free, difficult to prepare. Principal compounds, the chlorid and carbonate and other salts.

Magnesium, atomic weight 24.—Gray, malleable, does not occur free, burns with a dazzling light. Principal compounds, the oxid, carbonate, sulfate, and chlorid.

Calcium, atomic weight 40.—Soft, white, very active, does not occur free. The principal compound is calcium carbonate or limestone.

Barium, atomic weight 137.—Dark yellow solid, difficult to separate, oxidizes easily, does not occur free. Principal compound, heavy spar or barium sulfate.

Aluminum, atomic weight 27.—Bluish white, malleable, very light, not active, difficult to separate, a useful metal. Compounds, clay, alum, and many aluminum silicates.

Iron, atomic weight 56.—The most useful and most abundant of the common metals, gray, hard, strong, malleable, ductile, does not occur free. Principal compounds, the oxid, sulfid, and carbonate.

Manganese, atomic weight 55.—Black, does not occur free, not very active, acts both as a metal and a non-metal, often associated with iron ores.

Chromium, atomic weight 52.4.—Steel-gray, does not occur free, difficult to separate, often associated with iron ores. Compounds, chrome yellow or lead chromate and potassium dichromate.

A few other elements, though occurring in smaller quantities, are worthy of mention here.

Gold, silver, and platinum, called the noble metals, are unchanged in the air, take a fine polish, have beautiful color, and are used for making jewelry, coins, and vessels for special purposes.

Mercury, the only liquid metal, white, heavy, used in barometers and thermometers.

Lead, copper, zinc, and *tin* are useful metals, malleable, ductile, of characteristic color, lead gray, copper red, zinc bluish, and tin white.

PREPARATION OF THE ELEMENTS.

There are three general methods of preparing the elements:

1. *By electrolysis.* The electric current carries the ions to the electrodes, where they lose their charge and are separated as elements, provided they are not acted upon by the electrode nor the solvent.

2. *By thermolysis.* When one of the parts into which a compound is decomposed by heat is an element, and it or the other part can be removed so as to prevent reunion, the free element is obtained.

3. *By chemical displacement.* On heating an element with a compound, the element of the compound is sometimes displaced, the action being generally, no doubt, one between ions. This is the method most commonly used, and the more important elements which serve for the displacement are hydrogen, hydrogen ions, nascent hydrogen, chlorin, bromin, and metals like sodium, potassium, magnesium, aluminum, iron and carbon.

ORDER OF TREATMENT.

According to the periodic classification the elements may be placed in the following groups:

1. Hydrogen.
2. The helioids.   Group VIII B.
        Helium, neon, argon, krypton, xenon.
3. The chloroids or halogens.   Group VII B.
        Fluorin, chlorin, bromin, iodin, thulium.

4. The manganoids.   Group VII A.
  Manganese, samarium.
5. The sulfoids.   Group VI B.
  Oxygen, sulfur, selenium, tellurium.
6. The chromoids.   Group VI A.
  Chromium, molybdenum, neodymium, tungsten, uranium.
7. The nitroids.   Group V B.
  Nitrogen, phosphorus, arsenic, antimony, erbium, bismuth.
8. The vanadoids.   Group V A.
  Vanadium, columbium, praseodymium, tantalum.
9. The carboids.   Group IV B.
  Carbon, silicon, germanium, tin, lead.
10. The titanoids.   Group IV A.
  Titanium, zirconium, cerium, thorium.
11. The boroids.   Group III B.
  Boron. aluminum, gallium, indium, terbium, thallium.
12. The scandoids.   Group III A.
  Scandium, yttrium, lanthanum, ytterbium.
13. The glucinoids.   Group II A.   Alkali earth-metals.
  Glucinum, magnesium, calcium, strontium, barium.
14. The zincoids.   Group II B.
  Zinc, cadmium, mercury.
15. The potassoids or lithioids.   Group I A.   Alkali metals.
  Lithium, sodium, potassium, rubidium, cæsium.
16. The cuproids.   Group I B.
  Copper, silver, gadolinium, gold.
17. The ferroids, palladinoids, and platinoids.   Group VIII A.
    (a) Iron, nickel, cobalt; (b) ruthenium, rhodium, palla-
    dium; (c) osmium, iridium, platinum.

In the descriptive portion of this work the above scheme is
followed so far as possible.   In order to introduce some typical ele-
ments first and to secure an exhaustive treatment of the compounds,
a slight departure was necessary.   Hydrogen and oxygen and their
compounds water and hydrogen peroxid are considered first.   Then
the elements are taken by groups, beginning with the most negative,
and each one is described together with the compounds which it
forms with all the elements which have been treated before it.   The
chapters on the atmosphere and combustion are placed immediately
after the carbon group, and manganese is treated in close connection
with the ferroids.

CHAPTER XVII.

HYDROGEN.

Symbol H. Valence I. Atomic weight 1. Density 1. Molecular formula H_2. Molecular weight 2. Specific gravity 0.0696. Liter weighs 0.0899 gram (1 crith).

Occurrence.—Hydrogen, because of its chemical activity, and especially because of its affinity for oxygen, occurs free on the earth in very small quantities, and then only where chemical processes are going on which set it free. It is found in gases coming from volcanoes and oil-wells and some coal-mines. It is sometimes set free in the decomposition of organic matters and may thus occur in the breath and intestinal gases of animals. The spectroscope shows it to exist in the fixed stars, in some nebulæ, and in the photosphere of the sun. The prominences seen projecting for millions of miles from the sun's disk during solar eclipses are composed mainly of incandescent hydrogen. Meteorites often contain occluded hydrogen.

Combined hydrogen occurs abundantly in nature. Its most important compound is water, of which it constitutes one ninth by weight. It is found in nearly all organic substances and in many minerals, and is an essential constituent of all acids and bases.

History.—In the sixteenth century Paracelsus observed that an inflammable gas was given off when metals were acted on by acids. Cavendish discovered the true nature of this gas in 1766, and in 1781 he and Watts showed that water was the result of its combustion in the air. Lavoisier gave it the name *hydrogen* from the Greek which means *water-producer*.

Preparation.—Hydrogen is obtained from its compounds by decomposing them in such a way that there is nothing else present

182

with which it can unite.   The methods of preparation are numerous and only a few are given:

1. By the electrolysis of hydrogen compounds, as in the reactions,

$$H_2O = H_2 + O \ . \ . \ . \ (1) \qquad HCl = H + Cl \ . \ . \ . \ (2)$$

2. By action of intense heat, as when melted platinum is dropped into water. (Equation 1.)

3. By action of metals upon water; sodium or potassium at the ordinary temperature:

$$Na + H_2O = NaHO + H. \ . \ . \ . \ . \ . \ . \ . \ (3)$$

or at the boiling-point, zinc which has been coated with copper by dipping it in solution of copper sulfate (zinc-copper couple):

$$Zn + H_2O = ZnO + H_2. \ . \ . \ . \ . \ . \ . \ . \ (4)$$

or iron at red heat:

$$Fe_3 + 4H_2O = Fe_3O_4 + 4H_2. \ . \ . \ . \ . \ . \ . \ (5)$$

4. By the action of metals on acids; as,

$$Fe + 2HCl = FeCl_2 + H_2. \ . \ . \ . \ . \ . \ . \ . \ (6)$$

$$Zn + H_2SO_4 = ZnSO_4 + H_2. \ . \ . \ . \ . \ . \ . \ (7)$$
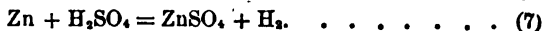
5. By action of metals on bases; as,

$$Mg + 2KHO = Mg(OK)_2 + H_2. \ . \ . \ . \ . \ . \ . \ (8)$$
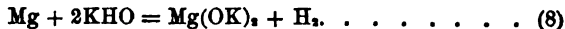
6. By destructive distillation of organic compounds, as in coal-gas.

7. By passing steam over charcoal heated to redness:

$$C + 2H_2O = CO_2 + 2H. \ . \ . \ . \ . \ . \ . \ (9)$$

The common and most convenient method of preparing hydrogen is by the action of zinc on sulfuric acid. (Equation 7.) Strips of sheet zinc or, better, fragments of granu-lated zinc (prepared by pouring melted zinc in cold water) are placed in a bottle furnished with funnel and delivery tubes. The delivery tube passes beneath the re-ceiver on the water-cistern, or communi-cates by means of a rubber tube with a gasometer. Sulfuric acid diluted with five or six volumes of water, specific gravity 1.18, is poured through the funnel-tube and the gas, which is rapidly evolved, escapes

FIG. 47.

through the delivery tube.   The gas should not be collected until all the air is expelled from the bottle.
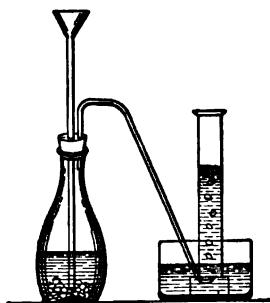
Purification.—Hydrogen thus prepared contains impurities derived from the materials used, such as hydrogen sulfid, hydrogen phosphid, hydrogen arsenid, sulfurous oxid, nitrous fumes, and certain hydrocarbon compounds. These may be removed by passing the gas through a series of U tubes containing substances to absorb them. Lead nitrate in the first removes the hydrogen sulfid, silver sulfate in the second absorbs the hydrogen arsenid and hydrogen phosphid, charcoal in the third removes the hydrocarbons, while the moisture and other impurities are retained in tubes containing potash, calcium chlorid, sulfuric acid, and phosphoric oxid.

A simple though rather expensive method of preparing hydrogen is by the action of sodium upon water. The metal by its superior affinity for oxygen displaces one half the hydrogen of the water. (Equation 3.) Heat enough is generated by the action to melt the sodium, which, being lighter than water, runs about on the surface as a silvery globule. If the water be warm, or the globule be held in one place by dropping a piece of paper upon the surface of the water, the escaping hydrogen takes fire and burns with the bright yellow flame characteristic of sodium. In order to collect the hydrogen, the piece of sodium is caught in a wire cage and depressed beneath the mouth of a test-tube filled with water and inverted over the water-cistern. By using a little dexterity the sodium may be introduced beneath the test-tube with pincers.

Pure hydrogen may be prepared according to equation 8 above, or by the electrolysis of acidulated water. In the latter process a glass decomposing cell is used, the positive electrode being amalgamated zinc, and the negative a leaf of platinum. The oxygen is retained by the zinc, forming zinc sulphate.

Caution.—However hydrogen is prepared, care must be taken that it be free from air, for the two together make a violently explosive mixture. Before collecting the hydrogen for use, time must be allowed for all the air to be expelled from the vessel in which it is being generated. In order to test it, fill a large test-tube with the gas and bring the mouth of the tube to a flame. If the hydrogen burns quietly, it is free from air; if it makes a slight explosion, further time must be allowed. The hydrogen in the gasometer should be so tested every day before it is used.

Physical Properties.—Hydrogen is a colorless gas with neither odor nor taste. It is the lightest substance known, its specific gravity being 0.0696. It is the standard of vapor density, atomic weight, molecular weight, molecular volume, diffusibility, and val-

ence. The weight of one liter at 0° and 760 mm. is called a *crith* (Greek, a *barleycorn*) and is equal to about 0.0899 gram. This number varies with the latitude. At Paris it is 0.089578 gram. One gram of hydrogen occupies a volume of 11.12 liters. The diffusibility of hydrogen is greater than that of any other gas. The estimated mean velocity of the hydrogen molecules at standard conditions is 1844 meters per second. It diffuses readily through the pores of red-hot metals such as iron, platinum, and · palladium. The velocity of sound is increased in it and its intensity much diminished. Its refractive power compared with that of air is 6.6. It is but slightly soluble, 100 volumes of water dissolving only about 2 volumes at 0° and 1.8 volumes at 20°. It is somewhat more soluble in alcohol.

Hydrogen is the most difficult of all· gases to liquefy except helium. Its critical temperature and pressure are −225° and 15 atmospheres. When condensed it is a colorless liquid which boils at −252° and has a specific gravity only 0.07 (Dewar). It is therefore the lightest liquid known. In the cold produced by its own evaporation when the pressure is suddenly reduced, it becomes a transparent solid which melts at about −257°, or within 16° of absolute zero. It thus furnishes the most intense cold that has ever been obtained. It was first liquefied by Olszewsky in 1895.

The spectrum of hydrogen consists of four bright lines, one in the red corresponding to the Fraunhofer line C, one in the blue coincident with the dark line F, and two in the indigo.

Many metals and some other solids have the power of absorbing or occluding hydrogen. Charcoal absorbs 2 volumes, finely divided iron 20 volumes, and platinum sponge 50 volumes. Palladium at red heat absorbs 935 volumes, increasing nearly one tenth in bulk, and when cooled still retains 376 volumes. The appearance of the metal is not changed, but its tenacity, its power of conducting heat and electricity, and its specific gravity are diminished, while its magnetic power is increased. The hydrogen thus occluded is called *hydrogenium* and has a calculated specific gravity 0.62.

Illustrations.—The lightness of hydrogen may be shown as follows :

(*a*) Fill soap-bubbles from the end of a rubber tube or from a clay pipe moistened with a soap solution with hydrogen from the gas-bag or -holder. As the bubbles become detached they rise rapidly to the ceiling.   .

(*b*) Fill a jar with the mouth down with hydrogen and pour it upward

into another jar. A burning match will show which jar contains the hydrogen.

(c) Suspend a light beaker mouth down from one end of a balance-beam and counterpoise it with weights. Pour a jar of hydrogen up into the beaker.

The effect of hydrogen upon sound may be shown by passing a sounding-fork or a squeaking toy up into a jar filled with the gas.

The diffusibility of hydrogen has been illustrated.

Chemical Properties.—Hydrogen at the ordinary temperature is quite inactive and its compounds are rather unstable, particularly because of its strong affinity for the oxygen of the air. At high temperatures, or in its nascent state, or in occlusion it is chemically quite active, entering into combinations which it would not otherwise form, and acting as a powerful reducing agent.* It unites directly to most of the elements which are negative to it, but rarely to the others. It unites indirectly to almost all the elements forming ternary compounds, the most important of which are the acids and bases. With nitrogen it enters into that large class of compounds called ammonia derivatives, and with carbon is a constituent of the innumerable substances of organic chemistry.

Hydrogen takes fire at about 500° and burns with great vigor, uniting with the oxygen of the air to form water. The flame is pale blue and scarcely luminous, but brightens under pressure. The heat of the combustion is very great, one gram of hydrogen yielding 34,462 heat-units. The temperature of hydrogen burning in air is, according to Bunsen, 2024°; in oxygen, 2844°. Mixtures of hydrogen with air, oxygen, chlorin, or vapor of bromin explode with violence on being ignited.

Hydrogen does not support ordinary combustion. A lighted taper is extinguished in it because the materials of the taper will not unite with it. A jet of oxygen or chlorin burns freely in an atmosphere of hydrogen.

Illustrations.—Introduce a lighted candle into a cylinder of hydrogen held mouth down. The gas takes fire and burns at the mouth of the cylinder; the candle is extinguished, but on being withdrawn is relighted as it passes out through the burning hydrogen. This shows that hydrogen is a combustible, but not a supporter of combustion.

---

* A reducing agent is one which takes oxygen from its compounds. All combustibles are reducing agents.

Ignite a jet of hydrogen coming from the generator, or, better, from a gas-bag or gas-holder. The jet may be of platinum or simply a glass tube drawn out so as to leave a fine opening. Note the character of the flame. If glass is used, the flame will soon become yellow because the glass becomes red-hot.

The formation of water is shown by letting the jet burn in a glass tube. Drops of water collect on the cold wall of the tube.

If the tube is of proper size, 1 to 2 cm. in diameter and 30 to 50 cm. long, a musical tone will be heard whose pitch will depend upon the length of the tube. The sound is produced by a quivering motion of the flame.

The great heat of the flame is shown by introducing thin strips of metal. They easily melt, giving the flame characteristic colors. Platinum does not melt, but colors the flame at first a bright yellow.

The reducing action of hydrogen is shown by passing it through a tube containing red-hot copper oxid; copper is separated :

FIG. 48.

$$CuO + H_2 = Cu + H_2O.$$
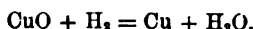
To show the activity of nascent hydrogen, place in a beaker some zinc and some silver chlorid and cover them with dilute hydrochloric acid. In a short time silver will be deposited, the nascent hydrogen having taken the chlorin to form HCl.

To illustrate the explosive mixture of air and hydrogen, we may use the "hydrogen pistol," a tin flask of about a liter capacity with a small aperture in the side near the base. Cover the aperture with the finger and fill the flask mouth down with hydrogen. Remove the finger and light the gas at the aperture. As the escaping gas burns, the air enters below and mixes with the hydrogen in the flask. Presently the flame enters and the mixture burns with a loud explosion. The explosion may be brought about sooner by turning the mouth of the flask upward after the gas has burned for a few moments.

Physiological Properties.—Hydrogen does not support respiration; animals smother in it for want of oxygen. It is not poisonous. An animal will breathe without inconvenience for a time a mixture of 4 parts of hydrogen and 1 part of oxygen.

Uses.—Hydrogen is used as follows:

1. On account of its lightness, for filling balloons, one liter having an ascensional force of about 1.2 grams.
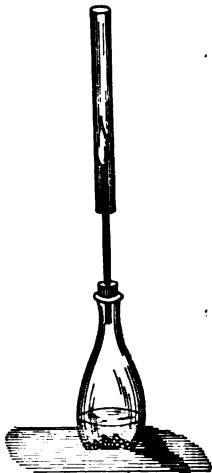
2. As a source of high heat in certain metallurgical operations, as in melting platinum.

3. For the production of the calcium light. For this purpose, however, ordinary coal-gas is generally used, as it is cheaper and more convenient.

4. As a reducing agent, and in various laboratory operations.

Tests.—Hydrogen is recognized by its lightness, its ready union with chlorin, its combustibility, and the nature of the product of its combustion.

Hydrogen Ion.—Acids and some other compounds dissociate, yielding the hydrogen ion $H\cdot$. This ion is univalent, colorless, poisonous, very active, and a powerful catalytic agent. It is the characteristic ion of all acid solutions, and acid properties are probably wholly due to it. It readily gives up its electric charge to metals assuming the molecular condition and appearing as elemental hydrogen. This seems to be the real reaction when metals are brought in contact with acids. In the following reaction,

$$2H\cdot + 2Cl' + Zn = Zn\cdot\cdot + 2Cl' + H_2,$$
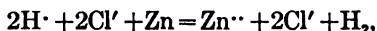
the electric charge is transferred from the hydrogen to the zinc, and the chlorin ions remain unchanged. The heat of formation of the hydrogen ion from molecular hydrogen is very small, about -900 calories, and for practical purposes is assumed to be zero. The heat of formation of an acid is then equal to that of the anion, and this assumption furnishes a means of determining the heat of formation of ions generally.

CHAPTER XVIII.

OXYGEN.

Symbol O. Valence II. Atomic weight 16. Density 16. Molecular formula O_2. Molecular weight 82. Specific gravity 1.106. Liter weighs 1.43 grams.

Occurrence.—Of all the elements oxygen is the most widely diffused and the most abundant. It exists free in the atmosphere, of which it is one fifth, and in solution in all terrestrial waters. It is also a constituent of the atmosphere of the sun. Combined, it constitutes nearly one half of the solid crust of the earth, eight ninths of water, and three fourths of all animals and plants.

History.—Oxygen was discovered by Priestley in England in 1774 and independently by Scheele in Sweden in 1775. A little later Lavoisier, in France, discovered the rôle it plays in respiration and combustion and gave it the name *oxygen*, which is Greek and means *acid-maker*. The negative oxids make acid solutions, and were themselves formerly called acids.

Preparation.—Although oxygen is the most abundant of the elements, it is quite difficult to get it pure except in small quantities. It may be obtained by separating it from the nitrogen of the air, or by the decomposition of oxids, and salts rich in oxygen. The following are some of the methods:

1. By heating the oxids of mercury, manganese, lead, barium, chromium, etc.

$$HgO = Hg + O \quad . \quad . \quad . \quad (1) \qquad MnO_2 = MnO + O \quad . \quad . \quad . \quad (2)$$

2. By the decomposition of water (a) by melted platinum, (b) by electricity, (c) in the form of steam by chlorin:

$$H_2O = H_2 + O \quad . \quad . \quad . \quad (3) \qquad H_2O + 2Cl = 2HCl + O \quad . \quad (4)$$

3. By the action of sunlight on carbon dioxid in the leaves of plants:

$$CO_2 = C + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

4. By the action of heat upon various salts:

$$2KClO_3 = KClO_4 + KCl + O_2 \quad (6) \qquad KClO_3 = KCl + 3O \quad (7)$$
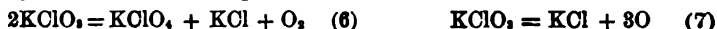
5. By the action of sulfuric acid on higher oxids and salts:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O \quad \ldots \ldots \quad (8)$$

$$K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \ldots \quad (9)$$
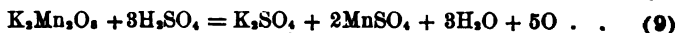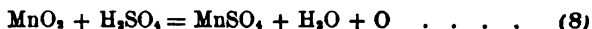
6. By the catalytic action of cobalt oxid upon bleaching-powder:

$$Ca(OCl)Cl = CaCl_2 + O \quad \ldots \ldots \ldots \ldots \quad (10)$$

7. By dropping sulfuric acid upon red-hot bricks (Deville):

$$H_2SO_4 = H_2O + SO_2 + O \quad \ldots \ldots \ldots \ldots \quad (11)$$

8. When barium oxid is heated in the air it becomes barium dioxid. At a higher temperature or under diminished pressure it separates again into barium oxid and oxygen (Bousingault):

$$BaO + O = BaO_2 \ldots \ldots \quad (12) \qquad BaO_2 = BaO + O \ldots \ldots \quad (13)$$

9. Cuprous chlorid when heated in the air becomes cupryl chlorid, and at a higher temperature gives up the oxygen again (Mallet):

$$Cu_2Cl_2 + O_2 = 2CuOCl \quad (14) \qquad 2CuOCl = Cu_2Cl_2 + O_2 \quad (15)$$

10. By heating sodium or potassium manganate to redness in a current of steam oxygen is set free. On heating the residue in the air oxygen is absorbed again (Tessie du Motay):

$$2Na_2MnO_4 + 2H_2O = Mn_2O_3 + 4NaHO + 3O \quad \ldots \ldots \quad (16)$$

$$Mn_2O_3 + 4NaHO + 3O = 2H_2O + 2Na_2MnO_4 \quad \ldots \ldots \quad (17)$$
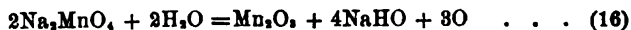
The last four processes are used for the preparation of oxygen on a large scale.

For common purposes oxygen is always prepared from potassium chlorate. This compound melts at 400° and gives up its oxygen with a brisk effervescence. (Equations (6) and (7).) If it be mixed with one fourth its weight of manganese dioxid, the whole of the oxygen comes off at about 200°, which is below the melting temperature of the chlorate. The manganese dioxid remains unchanged, its action being a catalytic one. In reality a series of reactions is supposed to take place represented by the following equations:

$$2MnO_2 + 2KClO_3 = 2KMnO_4 + Cl_2 + O_2$$
$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$
$$K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2$$
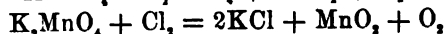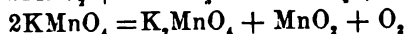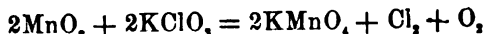
The materials are heated in a flask or retort of metal or hard glass, and the oxygen is collected over water or conveyed into a gasholder. The oxygen thus obtained is liable to contain carbon dioxid

and chlorin.   These may be removed by passing the gas through a solution of potassium or sodium hydroxid.

In small quantity oxygen may be prepared by heating mercuric oxid in a hard glass tube. (Equation 1.) The mercury condenses on the tube and the oxygen passes out.   A delivery-tube may be attached and the gas collected over water.   This is the classic
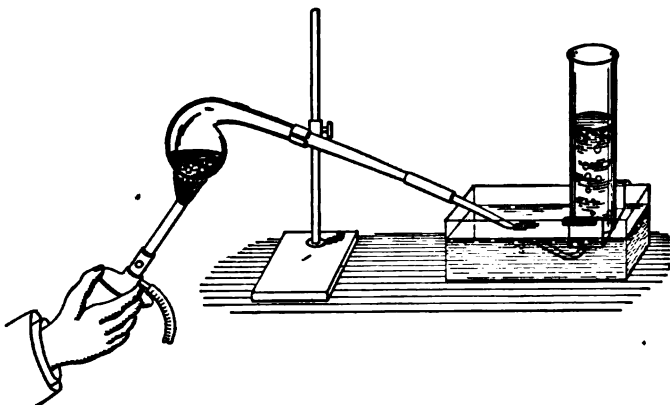
FIG. 49.

experiment by which oxygen was first prepared by Priestley, August 1, 1774.   He heated the oxid by condensing the rays of the sun with a powerful burning-glass.

Physical Properties.—Oxygen is a colorless, odorless, tasteless gas, a little heavier than the air, its specific gravity being 1.1056. A liter weighs under standard conditions 1.43 grams.   Its refractive power is less than that of any other gas, being to that of air as 0.8616 to 1.   It is quite strongly magnetic.   Its atomic weight referred to hydrogen is, according to determinations of Morley, 15.879.   It is frequently used as the standard of atomic weight with the weight 16.

Oxygen is slightly soluble in water.   Its coefficient of solubility at 0° and 760 mm. is 0.041.   At the ordinary temperature 100 volumes of water dissolve about 3 volumes of oxygen.   It is more soluble in alcohol, 100 volumes dissolving 28.

Oxygen is easily liquefied under moderate pressure at the very low temperatures now available.   Its critical temperature is − 118° and its critical pressure is 51 atmospheres.   It was first liquefied

independently by Pictet and Cailletet in 1877. The liquid is pale blue and limpid, and boils under atmospheric pressure at $-182°$, and *in vacuo* at the very low temperature of $-225°$. In ordinary vessels it boils violently even when immersed in liquid carbon dioxid, $-78°$, but in vacuum jacketed flasks or tubes it remains a quiet, static liquid, evaporating slowly. Its specific gravity varies with its temperature. At its boiling-point, $-182°$, it is a little heavier than water, having a specific gravity 1.124. As the temperature rises the density diminishes rapidly, being 0.87 at $-139°$, 0.81 at $-134°$, 0.75 at $-129°$, and 0.65 at $-118°$. Cooled by its own evaporation *in vacuo* it becomes a white solid.

Certain metals in a state of fusion absorb oxygen and give it out again on cooling. Silver absorbs about ten volumes, and the escaping gas causes the *spitting* of cooling silver.

Chemical Properties.—Oxygen is the most active of all the elements, with the possible exception of fluorin and chlorin. The only element which can resist its action is fluorin. It unites with all the others to form oxids, and when pure and aided by heat its action is most vigorous. Its activity is greatly reduced in the air by its admixture with four times its volume of nitrogen. Its union with other elements is called oxidation and is always attended with heat and often with light.

Most oxidizable substances undergo slow oxidation or combustion in the air. The rusting of metals and decay of organic matters are examples. Moisture aids in this action, and in most cases its presence seems to be a necessary condition. It may be the real oxidizing agent, but the action is more probably a catalytic one. Even at high temperatures oxidation does not easily begin without moisture. It is said that phosphorus may be distilled without taking fire in perfectly dry air or oxygen. The introduction of even a trace of moisture causes it to burst into flame.

An *oxidizing agent* is one which causes oxidation. Not only oxygen itself is such an agent, but many of its compounds are also. They may be even vigorous supporters of combustion, as, for example, hyponitrous oxid, N_2O. Among the common oxidizing agents are the peroxids and persalts, and the oxids, acids, and salts of nitrogen, chlorin, bromin, and iodin. Substances which contain no oxygen may be indirectly oxidizing agents. Such are the halogens and the haloid acids in the presence of water. They act by taking the

hydrogen from the water and setting free active nascent oxygen. We may classify oxidizing agents as follows:

1. Oxygen and ozone.
2. Compounds rich in oxygen and unstable.
3. Substances able to set oxygen free from water or other compounds.

Illustrations.—The effect of oxygen upon combustion may be shown in various ways. In oxygen, a splinter with a spark on the end bursts into flame, charcoal burns vividly, sulfur burns with a bright blue flame, and heated sodium and potassium take fire spontaneously. Still more brilliant experiments are made by burning iron and phosphorus.

Remove the temper from a small watch-spring by heating it to redness. Pass it through a jar-cover and attach to its end the point of a match or dip it in melted sulfur. Light and lower it quickly in a jar of oxygen. The wire will burn with bright scintillations and molten globules of iron tetroxid, Fe_3O_4, will fall to the bottom of the jar, melting into the glass. The bottom may be covered with sand or water to keep the jar from being broken.

This experiment may be varied as follows: Let a jet of oxygen pass through the flame of a lamp and hold in the flame a bundle of small steel wires. As soon as the wire is red-hot it burns in the jet of oxygen.

Place a small bit of sulfur or phosphorus in a combustion-spoon (this may be made by attaching a piece of chalk crayon to a wire), ignite and lower in a jar of oxygen. The sulfur flame is a deeper blue than in the air. The phosphorus is volatilized by the heat and burns throughout the jar with dazzling brilliancy. The products of the combustion are SO_2 and P_2O_5.

Physiological Properties.—The oxygen of the air is the supporter of animal life. Undiluted oxygen may be breathed for a time, but soon produces bad effects. Compressed oxygen acts as a poison, causing death very quickly.

Respired air has gained 3 to 4 per cent of carbon dioxid and lost 4 to 5 per cent of oxygen. The oxygen passes into the system through the blood. A substance in the blood called *hæmoglobin* combines with the oxygen to form *oxyhæmoglobin*. In this form oxygen is carried to the tissues of all parts of the body, where it is used in oxidizing carbon and hydrogen, and thus developing the heat and energy which are necessary to life and activity.

Uses.—The uses of oxygen are almost innumerable. In nature it is the supporter of combustion and respiration. Animals obtain it from the air, and dissolved oxygen supports aquatic life. The heat and light of combustion are utilized in ways familiar to all.

Undiluted oxygen is used in the arts for accelerating combustion and securing intense heat and light. It is also used as a medicine, being administered in cases of difficult breathing, as in croup, asthma, and asphyxia. In the form of ozone it is a powerful disinfectant.

Oxygen, in connection with some other elements, is the chief vehicle for the transmission of energy in the organic world. In entering combinations it sets free energy, and in leaving combinations it stores up a like amount of energy. By the influence of sunlight on the leaves of plants oxygen is set free and energy stored in the tissues of the plant. This energy is given out again in the burning of the fuel, thus running our engines and lighting and warming our houses. This energy is also utilized in the assimilation of food, the oxygen here recombining and developing that force which is manifested in the movements of living beings.

Tests.—Free oxygen causes a glowing splinter to burst into a blaze. Passed over heated metals it oxidizes them. It is absorbed by an alkaline solution of pyrogallic acid.

Illustration.—Into a long tube containing a few cubic centimeters of potassium hydroxid solution drop a few flakes of pyrogallic acid. Cover the mouth of the tube with the thumb, shake, invert in a vessel of water and remove the thumb. The water rises in the tube to take the place of the oxygen absorbed. The result will be more striking if the tube be first filled with oxygen.

Oxids.—Oxids are somewhat arbitrarily divided into two classes, the negative oxids, called also anhydrids, and the positive oxids.

The negative oxids, or oxids of the negative elements, are gases, liquids, or solids, usually amorphous, which form acid solutions in water. Examples are sulfurous oxid, SO_2, gas, and phosphoric oxid, P_4O_5, solid. With water they form sulfurous and phosphoric acids:

$$SO_2 + H_2O = H_2SO_3, \qquad P_2O_5 + H_2O = 2HPO_3.$$

The positive oxids, or oxids of the positive elements, are mostly amorphous solids soluble or insoluble in water. The solutions are bases and are called *hydroxids*. Examples are potassium oxid, K_2O, potassium hydroxid, KHO, calcium oxid, CaO, calcium hydroxid, $Ca(HO)_2$.

OZONE.

Formula O₃.   Molecular weight 48.   Density 24.·

Formula O_3.   Molecular weight 48.   Density 24.·

Occurrence.—Ozone occurs in small but varying quantities in the atmosphere.   It is most abundant at sea and in the country.   It is almost entirely wanting in city atmospheres, because the organic matters decompose it as fast as it is formed.   The quantity in the air is increased during thunder storms and about electric machines.

History.—Ozone was first noticed by Van Marum in 1785 in electrified air.   In 1840 Schönbein called attention again to this substance, discovered its oxidizing action, and showed that it was produced in the electrolysis of water and in slow combustion of phosphorus and sulfur.   He gave it the name *ozone*, which means a *smell*.   The investigations of De la Rive, Becquerel, Tait, Fremy, Andrews, and Brodie have proved it to be modified oxygen.   Its density was determined by Soret in 1860.

Preparation.—Ozone is formed in a great variety of ways, among which are the following:

1. By the action of intense heat upon oxygen, as when a spiral of platinum is heated in the air.

2. By the evaporation of water.   This accounts for the large amount of ozone in the sea-breeze.

3. By the action of sunlight upon the essential oils.

4. In the decomposition of carbon dioxid in the leaves of plants the oxygen set free contains ozone.

5. By the electric discharge in the air or in oxygen.

6. In the electrolysis of acidulated water some ozone is evolved at the positive electrode.

7. By slow combustion when the supply of oxygen is abundant.

8. By the action of a strong acid, such as sulfuric acid, upon highly oxygenized bodies, such as barium peroxid and potassium permanganate.

For the preparation of ozone by the electric discharge a Siemens induction-tube is used.   This consists of a glass tube coated with tin-foil on the inside and surrounded by another tube coated with tin-foil on the outside.   The outer and inner coatings are connected with the wires of an induction-coil, and as the current passes a stream of air or oxygen is passed between the tubes. · The gas comes out strongly ozonized.   In the simpler apparatus shown in the figure one platinum wire penetrates the tube, while the other is coiled around it.

The formation of ozone by slow combustion may be shown by placing pieces of phosphorus in the bottom of a flask and half covering them with water or·a solution of potassium dichromate. The air in the flask will soon smell of ozone. It may also be shown as follows: Pour a few drops of ether into a tall beaker in which is suspended a strip of ozone test-paper. Lower in the beaker a glass rod which has been heated nearly to redness. Ozone is formed by the slow combustion of the ether and the test-paper is colored. The test-paper is made by dipping strips of paper in potassium iodid starch solution.

The liberation of ozone by chemical action may be shown by adding barium dioxid or potassium permanganate to a little strong sulfuric acid in a flask or bottle. In a few minutes the air in the vessel smells strongly of ozone.

Physical Properties.—Ozone prepared as above is largely diluted with oxygen or air. Only about twenty-five per cent of oxygen can be converted into ozone by the electric current.

Ozone is a gas with a faint blue color and a penetrating chlorin-like odor. It has not been obtained free from oxygen, but Soret found its density by observing the amount of condensation which a given quantity of oxygen undergoes and the amount of ozone produced, and also by the rate of its diffusion. The density thus found was 24. Its molecular formula is therefore O_3, with a probable structure $\overset{O}{\underset{O—O}{\diagup\diagdown}}$. It gradually passes back to oxygen, and at 250° the change takes place at once. It is slightly soluble in water, but in passing into solution it is mostly decomposed. Two hundred volumes of water dissolve one volume of ozone.

Liquid ozone is obtained by passing ozonized oxygen through a small tube immersed in boiling oxygen (− 182°). It is of a deep blue color and boils at − 106°. It is unstable and liable to explode. If enclosed in a tube, it changes to a blue gas which becomes a liquid again in boiling ethylene.

Chemical Properties.—The chemical properties of ozone are simply those of oxygen greatly intensified. It is an energetic oxi-

dizing agent at the ordinary temperature. It attacks organic matters, even rubber and paper, and most metals are oxidized by its action. Silver and lead are made peroxids, and phosphorus, sulphur, and arsenic in the presence of moisture are converted into phosphoric, sulfuric, and arsenic acids. Ammonia is changed to nitric and nitrous acids, lower oxides are transformed into higher ones, and iodin is set free from potassium iodid. Mercury in its presence tarnishes at once and adheres to the vessel containing it. Hydrogen sulfid and organic gases in the atmosphere are decomposed by it. It bleaches vegetable colors, such as litmus and indigo, and turns alcoholic solution of guaiacum blue. Physiologically it is poisonous, irritating the mucous membrane.

Ozone is simply allotropic oxygen, in which three atoms have been condensed into one molecule. The action is endothermic, and this accounts for the instability of ozone and the difficulty of its formation. The thermal and volumetric equation of its formation is

$$O_2 \ + \ O \ = \ O_3 \ - \ 32{,}400 \text{ cal.}$$
$$2 \text{ vols.} \ + \ 1 \text{ vol.} \ = \ 2 \text{ vols.}$$
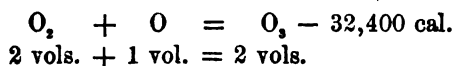
The activity of ozone is due to its instability and the ease with which it gives up one atom of its oxygen, $O_3 = O_2 + O$. This nascent oxygen atom or ion is the active oxidizing agent.

Illustrations.—Lower into a jar of ozonized air a bright silver coin. It tarnishes with formation of silver peroxid, Ag_2O_2. Repeat the experiment with mercury.

Pass ozonized air through solution of litmus or indigo.

Note the action on potassium iodid starch paper and on paper stained black by lead sulfid. The first is colored blue by the iodin which is set free, and the second is bleached by the conversion of lead sulfid into lead sulfate :

$$2KI + H_2O + O_3 = 2KHO + O_2 + I_2.$$
$$PbS + 4O_3 = PbSO_4 + 4O_2.$$
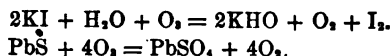
Uses.—In nature ozone acts as disinfectant, destroying noxious gases in the air. The tonic and curative effects of sea-breezes and mountain air are not due to the effect of ozone upon the system, but to its purifying influence upon the atmosphere. In the arts it has a limited use as a bleaching and oxidizing agent.

Tests.—Ozone is recognized by its odor, its bleaching and oxidizing actions, and its action with test-papers. The potassium-iodid-

starch and guaiacum papers are also blued by chlorin, bromin, nitrogen dioxid, and some other substances. To distinguish ozone from these, expose to the action of the gas a strip of red litmus paper which has been dipped in potassium iodid solution. If ozone is present, the potassium hydroxid formed will color the litmus blue.

Valence of Oxygen.—In all its ordinary combinations the valence of oxygen is two. Recent investigations show that in certain organic compounds it has the valence four. It has been suggested also that ozone may be an oxid of oxygen with the formula OO_2 or $O=O=O$, one of the oxygen atoms being tetravalent. It is probably the extreme negative quality of oxygen that prevents its acting with the higher valences.

Oxygen Ion.—Oxygen does not readily pass to the condition of the elemental ion O''. Its tendency is to unite with other elements to form complex ions. Solutions of the basic oxids contain the hydroxyl ion, or complex basic ions, such as $BiO\cdot$; while the acidic oxids yield the various acid ions, such as NO_3', SO_4'', etc. The heat of formation of the oxygen ion from molecular oxygen is 21,600 calories.

CHAPTER XIX.

OXIDS OF HYDROGEN.

THERE are two oxids of hydrogen with name, formula, and structure as follows :

Hydrogen oxid, water, H_2O or H—O—H.

Hydrogen peroxid, free hydroxyl, H_2O_2 or H—O—O—H.

The first is the regular saturated compound, and the second is formed by the union of two hydroxyl radicals, $(HO)_2$. In both formulas the valence of hydrogen is I and that of oxygen II.

WATER.

Formula H_2O. Molecular weight 18. Density 9. Specific gravity of vapor (air $=$ 1) 0.6208. Greatest density at 3.9°. Liter weighs 1000 grams. Boils at 100°. Freezes at 0°. Standard of specific gravity.

Occurrence.—Water is the most universally distributed and the most abundant of all substances. It saturates the soils, rocks, and atmosphere, and the excess rests upon the surface of the earth, making the oceans, lakes, and rivers. It penetrates all solid bodies, and there is absolutely nothing dry in nature.

Water may simply adhere to solids, or it may enter as a constituent. All solid surfaces are covered with a layer of moisture held by adhesive attraction. This is called *hygroscopic moisture*, and its quantity varies with the amount of moisture in the air. At 100° it is all expelled and the surface is left dry. It is for this reason that in accurate weighing the body is heated, and then cooled in a desiccator (a closed vessel with its contained air kept dry by strong sulfuric acid) before the weight is determined.

Water of constitution is not confined to the surface, but permeates the whole mass. It may be simply a loose molecular union, as in the case of water of crystallization, or it may be a closer chemical union,

199

as in the combination of water with oxids to make acids and bases, and in the case of the water contained in organic substances.

The per cent of water found in various associations is as follows :
Adherent moisture :

Soil......5 to 20 per cent   Dry earth......1 to 5 per cent

Water of crystallization:

Common salt at — 8°, $NaCl,2H_2O$.................38.1 per cent
Epsom salts, $MgSO_4,7H_2O$.........................52.5   "

Water of constitution and adhesion :

Dry wood.... 10 to 20 per cent   Green plants.. 75 to 90 per cent
Human body. 75 to 80   "   Beefsteak..... 75   "
Bread........ 30 to 40   "   Fruits........ 80 to 95   "

ι **History.**—Until near the close of the eighteenth century water was regarded as a simple or elementary substance. About 1781 Cavendish showed that when hydrogen and oxygen were burned together water was produced, and also that they united in about the proportion of two volumes of hydrogen to one of oxygen. In 1783 Lavoisier determined the composition of water by weight and obtained results which were not very far wrong. In 1805 the exact volume composition was determined by Gay-Lussac and Humboldt, and the ratio of combination by weight, one of hydrogen to eight of oxygen, was found by Berzelius and Dulong.

Preparation.—Water is one of the products of a great many chemical reactions, but because of its abundance free the methods by which it is formed are of simply scientific interest. The only one we need note here is its synthesis by the direct union of hydrogen and oxygen.

When hydrogen is burned in air or oxygen, water is the sole product of the combustion. As is indicated by the valence of hydrogen and of oxygen and by the formula of water, the gases unite exactly in the proportion of two volumes of hydrogen to one of oxygen and one part of hydrogen to eight of oxygen by weight. These facts are expressed in the equation

$$H_2 + O = H_2O. \qquad H_2 + O = H_2O.$$
$$2 + 16 = 18 \qquad 2 \text{ vols.} + 1 \text{ vol.} = 2 \text{ vols.}$$
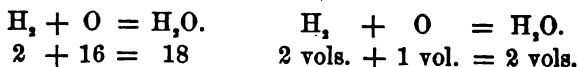
Three volumes become two, that is the steam formed only occupies two thirds the volume of the gases which formed it.

The reaction is intensely exothermic. The heat of formation of steam is 58,690 calories, and the heat of condensation of steam to

water is 9,670 calories.   The total heat of formation of water then
is

$$H_2 + O = H_2O + 68,360.$$

This means that in burning two grams of hydrogen heat enough is
evolved to raise 684 grams of water from 0° to 100°.

When a mixture of hydrogen and oxygen is ignited the gases
combine with a violent explosion and a deafening noise.   When the
two gases are burned together in the proper proportions from a jet
the temperature is the highest which can be obtained by combus-
tion, sufficient to melt platinum easily.   This is called the *oxyhydro-
gen flame.*   It was first used by Hare of Philadelphia in 1801.   If
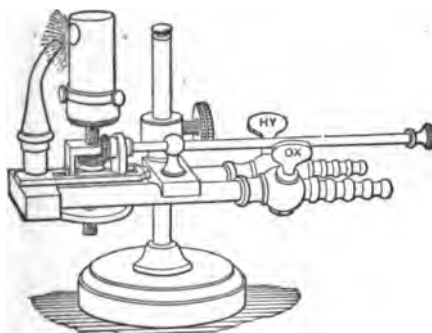
Fig. 51.—Lime-light.

this flame be allowed to play upon some infusible substance, as
quicklime, an intense white light is produced.   This is called the
lime-light, and is used for projecting pictures on the screen.

Illustrations.—To show the formation of water burn a jet of hydrogen
in a tube or under a bell-glass. The glass is immediately dimmed with
moisture, which soon collects in drops.

To show the detonation of the mixed gases fill a rubber bag half full of
hydrogen, then add half as much oxygen. Let the mixture flow out
through a tube into a dish of warm soapsuds so as to fill the dish with bub-
bles. Remove the bag to a distance and then apply a lighted taper to the
bubbles.

To show the action of the oxyhydrogen flame provide two gas-bags or
-holders filled the one with hydrogen and the other with oxygen, and an
oxyhydrogen blowpipe or jet. This is a jet with a platinum tip and a
small chamber at its base into which the gases are introduced and mixed
before passing out through the jet. The gases are made to flow by a gentle

pressure and so regulated by stopcocks as to insure the proper propor-
tions. The hydrogen is turned on first and lighted, then the oxygen is
slowly admitted. The flame is in its proper condition when it is reduced
to its smallest size and burns with a slight fringe of burning hydrogen.
Metals introduced into the flame melt at once and many of them burn vig-
orously. Platinum is melted, a watch-spring burns vividly, and small pieces
of cast iron held on charcoal yield brilliant scintillations. A small frag-
ment of lime or limestone gives the lime-light. City gas may take the
place of hydrogen.

Composition of Water.—The volumetric composition of water
may be demonstrated by both analysis and synthesis.

The analytic determination is made by electrolysis. Water acidulated
with one tenth its weight of sulfuric
acid is placed in a decomposing appara-
tus and a strong electric current passed.
The oxygen collects in the tube contain-
ing the positive electrode, and the hydro-
gen in the other. After the water has
become saturated with the gases the hy-
drogen tube will be seen to fill just twice
as rapidly as the oxygen tube.

For the synthesis of water an appa-
ratus called the eudiometer is employed.
This is a U tube with one limb closed
and carefully graduated and pierced with

Fɪɢ. 52.
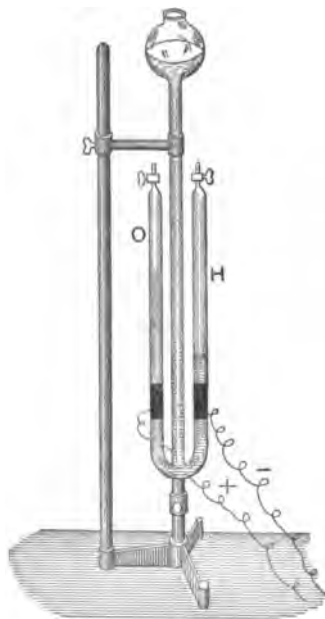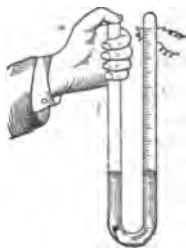
Fɪɢ. 53.

platinum wires which almost meet within. The tube is filled with mer-
cury and a side tube and stopcock permit the easy regulation of the
height of the mercury column. Oxygen is introduced by means of a tube
reaching to the bend of the eudiometer and the volume carefully noted on
the graduated tube. Rather more than twice as much hydrogen is now
introduced and the combined volumes noted. In every case before read-
ing the volume, the mercury must be adjusted to the same level in both

limbs in order that the volumes may be taken under the atmospheric pressure. Connect the wires with the poles of a Ruhmkorff coil, hold the thumb firmly over the open end of the tube and complete the circuit. The gases combine with explosion, the steam formed condenses to water, and the mercury rises in the tube. Adjust the level of the mercury and read the volume of the residual hydrogen. The small volume of water, produced may be neglected in this determination. It will be found that exactly two volumes of hydrogen and one of oxygen have disappeared. Example : 10 cc. of oxygen and 26 cc. of hydrogen were used and 6 cc. of hydrogen remained.

In order to determine the volume of steam produced the temperature of the apparatus must be raised above 100°. This is accomplished by enclosing the graduated limb with another tube and passing between them the vapor of some liquid which has a higher boiling-point than water, as amyl alcohol or anilin. After the explosion and the measurement of the residual hydrogen, the tube is heated until the water is all converted into steam and the steam has acquired the temperature of the surrounding vapor. The volume is measured, corrected from the temperature of the vapor (amyl alcohol about 180°) to that at which the first measurements were made, and the residual hydrogen subtracted; the remainder will be the volume of steam. It will be found to be two thirds of the volume of the hydrogen and oxygen used. There is a condensation of one third of the volume.

The composition of water by weight is conveniently determined by synthesis in the reduction of copper oxid, $CuO + H_2 = Cu + H_2O$. A weighed portion of the oxid is heated in a current of pure dry hydrogen and the water produced collected and weighed. The copper oxid is also weighed after the action. The loss in weight of the oxid is the oxygen used, and this subtracted from the water is the hydrogen. Example : 2.25 grams CuO lost 1.12 grams of O and formed 1.26 grams of H_2O. The H used was therefore $1.26 - 1.12 = 0.14$, and $0.14 : 1.12 :: 1 : 8$, the combining weights of hydrogen and oxygen. Since the molecule of water is 18, it must contain 2 of H and 16 of O, but 2 of H means 2 atoms and we have the formula H_2O.

Physical Properties.—Water is an odorless, tasteless, limpid liquid which boils at 100° and freezes at 0°. Its critical temperature is 370° and its critical pressure 195.5 atmospheres. It is practically colorless, but when viewed in large bodies by either transmitted or reflected light it is greenish blue. The color of terrestrial waters, lakes, rivers, and seas, is mainly due to suspended matters. Water is a poor conductor of heat, but better than any other non-metallic liquid. It is a bad conductor of electricity, and not an electrolyte until acidulated. It is slightly

compressible, 1000 volumes becoming 999.95 volumes under a pressure of one atmosphere. Its index of refraction is 1.3338.

Being abundant, stable, easily obtained in a very pure state, and presenting constant properties under constant conditions, water is well adapted for use as a standard. It is the standard for temperature, specific gravity, and specific heat, and is the basis for the metric system of weights, the gram being the weight of one cubic centimeter of water at its maximum density. Its capacity for heat is greater than that of any other substance, and all specific heats except that of water are fractions.

Water is almost a universal solvent. It is the most powerful of all ionizing agents. Its own dissociation into the ions H· and HO' is extremely small.

Purification of Water.—All natural waters contain impurities which give them their characteristic taste and quality. The most important dissolved substances are as follows:

Gases: Oxygen, nitrogen, carbon dioxide, and ammonia.

Liquids: Rarely found.

Solids: Organic matters and mineral matters. Of the latter the most common are carbonates and sulfates of calcium and magnesium, and chlorids of sodium and potassium.

Water may be almost entirely freed from solids by distillation, and may be kept so indefinitely in clean vessels. All the gases above mentioned are driven off at the boiling temperature, but are reabsorbed again on exposure of the water to the atmosphere. The first third of a distillate contains these gases, the last third is liable to contain gases resulting from the decomposition of organic matter, the middle third is practically free from solids and gases. To get water absolutely free from ammonia two or three distillations are necessary, the first and last thirds being rejected each time.

Illustrations.—Dissolved solids may be shown by evaporating a little well- or pipe-water to dryness in a dish. The dissolved gases separate in little bubbles as water approaches the boiling-point.

Water Vapor and Vapor Tension.—Water is volatile at all temperatures. Even ice slowly evaporates although its temperature be kept below 0°. The rapidity of evaporation increases with the temperature and diminishes as the pressure and the tension of the vapor already in the atmosphere increase. When the air is

saturated no evaporation takes place, or rather as many molecules
fall into the surface of the liquid as leave it. Air becomes
saturated under a certain tension which varies with the tempera-
ture. The tension at several temperatures in millimeters of
mercury is as follows: at − 10°, 2.1 mm.; at 0°, 4.6 mm.; at
10°, 9.2 mm.; at 20°, 17.4 mm.; at 50°, 92 mm.; at 100°, 760
mm., or 1 atmosphere; at 120.6°, 2 atmospheres; at 180°, 10
atmospheres; at 213°, 20 atmospheres; at 224.7°, 25 atmospheres;
at 370°, 195.5 atmospheres.

Steam.—On being heated to 100° water boils and is rapidly
converted into steam. The boiling-point, however, varies with
the pressure. The table of vapor tensions is at the same time a
table of boiling-points at the corresponding pressures. The heat
of vaporization is 536.5 calories; that is, in converting one gram
of water into steam enough heat is absorbed to raise 536.5 grams
of water through one degree. One volume of water at 100°
becomes 1696 volumes of steam at the same temperature.

Steam is a colorless gas, of which the theoretical density is 9.
At 100° and 760 mm. its specific gravity is 0.458, and a liter weighs
0.5922 gram. Steam is invisible; what is popularly known by the
name is the visible cloud formed by the condensation of the steam
into minute droplets of water.

Ice.—As water is cooled its volume diminishes and its density
increases until 4° is reached. On further cooling the volume
increases and the density diminishes to 0°, when it begins to
solidify. At 4°, then, or more accurately at 3.945°, water has its
greatest density. The actual change from 4° to 0° is about one
hundredth of one per cent. or one part in 10,000. The density is
the same at 0° that it is at 8°.

As water solidifies it expands about one tenth its volume, 100
volumes becoming 109.08 volumes of ice. The specific gravity of
ice is therefore 0.9167. The force of this expansion is enormous.
It causes the bursting of water-pipes and exerts a powerful influ-
ence in the disintegration of rocks in winter weather. As water
solidifies heat is given out, and as ice melts heat is absorbed to the
amount of 79 calories; that is, a gram of ice at 0° in melting to a
gram of water at 0° absorbs heat enough to raise the same gram of
water from 0° to 79°.

When a larger body of water is exposed to cold, the surface

layers increase in density and sink to the bottom. A circulation is thus set up which keeps the whole mass at about the same temperature until 4° is reached. Below this temperature the surface layers become lighter, float, cool rapidly, and freeze. As ice is added to the sheet below a large amount of heat of solidification is given to the underlying water and thus the freezing is retarded. The reason certain large bodies of water do not freeze is because the cold does not continue long enough for the whole mass to reach the 4° temperature. If water continued to contract on cooling, it would remain liquid until the whole reached zero and then would freeze solid.

Under certain circumstances water remains liquid at temperatures considerably below 0°. With diminished atmospheric pressure water may be cooled to − 12°; boiled water protected from dust to − 9°; Sorby cooled water in a capillary tube to − 15°; Boussingault lowered the temperature of water in a closed steel cylinder to − 24°. In these cases the slightest jar or the introduction of a solid particle causes instant solidification, the temperature rising at once to 0°.

While the freezing-point of water is liable to vary, the melting-point remains constant at 0°. Under increased pressure the melting temperature is lowered 0.0074° for each atmosphere.

Ice is transparent and colorless. In large masses it is greenish blue like water. It is a poor conductor of both heat and electricity. It is usually purer than the water from which it is formed, the solid matters being mostly rejected as the water freezes. Its refraction index at 0° is 1.333.

Ice crystallizes in rhombohedrons belonging to the hexagonal system. Snow crystals assume beautiful shapes and are mostly composed of needles taking the direction of the three horizontal axes of the hexagonal prism.

Chemical Properties.—Water is quite stable, but at the same time chemically very active. In connection with substances which combine with hydrogen, as chlorin, bromin, and iodin, it acts as an oxidizing agent. It is decomposed by many metals, as potassium, sodium, calcium, and iron, with the liberation of hydrogen. Dissociation begins at 1000°, but is only half complete at 2500°. It is a powerful catalytic and ionizing agent, and is itself ionized only to the extent of one mol in 10,000,000 liters.

The most important chemical action of water, however, is found in its direct union with other substances.   Three classes of compounds thus arise.

1. The union is a perfect chemical one, and the action is generally strongly exothermic.   This is illustrated by the union of positive and negative oxids with water to form bases and acids:

$$Na_2O + H_2O = 2NaHO + 55,000 \text{ cal.}$$
$$SO_3 + H_2O = H_2SO_4 + 21,400 \text{ cal.}$$
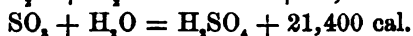
2. The union is a molecular one, as in the multitude of hydrates which may be obtained by the evaporation of solutions.   Here the water is usually present as water of crystallization, and the quantity is somewhat dependent upon the temperature at which the crystallization takes place.   Sodium carbonate at about 18° takes 10 molecules of water, Na_2CO_3, $10H_2O$, while at higher temperatures it takes 8, 7, or even only 5 molecules.

Many substances which crystallize at or above the ordinary temperature without water form hydrates at low temperatures. Such are called *cryohydrates*.   Common salt is ordinarily NaCl. Crystallized at − 7° it has the composition $NaCl,2H_2O$, and at − 23 it is $NaCl,10H_2O$.

3. Solutions.   These may be chemical unions, hydrates or mixtures, and it is hard to draw the line between them.   That there is generally chemical action is evidenced by the thermal changes. The action may be endothermic, but is more usually exothermic.

Tests.—Water is recognized generally by its physical properties. It gives a blue color with anhydrous copper sulfate.

Uses.—The uses of water are too manifold for enumeration. They may be classified as (1) chemical, (2) mechanical, (3) cleansing, and (4) nutritive.

1. The chemical uses of water have been sufficiently indicated under the head of Chemical Properties.

2. As a mechanical agent water is far-reaching in its effects. Geologically it has determined the present features of the earth. Through erosion, transportation, and deposit it has worn down mountains, cut out cañons and gorges, and filled up valleys and plains.   In the arts it is used both as a source of energy and as a transporting agent.

3. As a cleansing agent water is a necessity in domestic and public life. It is the sanitarian's strong right arm, and the scavenger which makes the modern city inhabitable.

4. As a nutritive agent it constitutes one of the most important of the foods of both plants and animals, and it is the carrier which brings all parts of the living body into communication.

Steam is a warming, solvent, and chemical agent, but its chief use is in the steam-engine as a source of power.

Ice is used mainly as a refrigerant. It is manufactured in large quantities for domestic use and is one of the greatest of modern luxuries.

Natural Waters.—All terrestrial waters are more or less impure. We may classify them according to the character and amount of dissolved matter into (1) *sea-waters,* (2) *mineral waters,* and (3) *fresh waters.*

1. *Sea-waters.*—One thousand grams of sea-water contains on an average about 35 grams of dissolved solids, chiefly sodium chlorid, and has a specific gravity 1.03. In certain inland lakes which have no outlet the mineral content is greatly increased by evaporation. The number of grams of dissolved solids in 1000 grams of several waters is as follows:

Mediterranean Sea	40.00	Elton Lake, Russia.	271.44
Dead Sea	228.57	Great Salt Lake, Utah	319.71

Sea-water from the British Channel contains in parts to 1000:

Sodium chlorid	27.059	Potassium chlorid	0.766
Magnesium chlorid	3.666	Calcium carbonate	0.033
Magnesium sulfate	2.296	Magnesium bromid	0.029
Calcium sulfate	1.406	Total solids	35.255

2. *Mineral Waters.*—These do not necessarily contain a large amount of dissolved matters, but rather have some one or more particular substances in excess, either gaseous or solid, which give the waters their peculiarities and often make them medicinal. These waters may be conveniently, though not very scientifically, classified according to the leading constituent into the following groups:

Carbonated waters, which contain much carbon dioxid and carbonates. They are often also strongly saline.

Sulfur waters, which have hydrogen sulfid in solution and are usually rich in sulfates.

Alkaline waters, which are rich in alkaline carbonates, especially sodium carbonate, and often contain much sodium chlorid and carbon dioxid.

Saline waters, in which sodium chlorid predominates. When this constituent is very high we have the regular salt waters or brines.

Calcic waters, which contain large amounts of calcium carbonate and calcium sulfate.

Magnesian waters, in which magnesium sulfate and carbonate are predominant.

Chalybeate waters, which contain salts of iron, especially the carbonate.

Silicious waters, which are rich in alkaline silicates. These waters are usually warm, as in the hot springs of Arkansas and Iceland.

Thermal waters, whose temperature is considerably above that of the atmosphere. These usually occur in volcanic regions, and the waters come from great depths where they have been in contact with hot rocks. All the above classes except the first may include warm waters.

The Saratoga waters are carbonated and saline ; the springs of Virginia, Tennessee, and Kentucky are many of them calcic, magnesian, sulfur waters ; many of the springs of Alabama, Mississippi, and Pennsylvania are chalybeate ; and warm springs are generally silicious.

3. *Fresh Waters.*—These may be conveniently classified according to the quantity of dissolved solids into (*a*) Rain-water, (*b*) Surface-waters, including lakes and rivers, (*c*) Spring and shallow-well waters, and (*d*) Deep-well waters.

a. Rain-water contains the smallest amount of solid matter, but is rich in gases dissolved from the atmosphere. Collected in the country it may contain as little as 2.9 parts solid matter to 100,000 parts of water, but in cities it may run as high as 7 parts to 100,000. It contains sodium chlorid, salts of ammonia, nitrates, organic matters, and often sulfuric acid.

b. The content in solid matter of lakes and rivers depends largely upon the rocks of the region in which they are located. In granite regions it may be as low as 4 parts, and among magnesian limestone rocks it may reach 50 parts, in 100,000. The Croton water which supplies New York City has 6 to 8 parts, the Cumber-

land River at Nashville has 11 parts, the Ohio River at Cincinnati has 14 parts, the White River at Indianapolis has 28 parts, Lake Michigan at Chicago has 14 parts, and Lake Katrine, Scotland, 3.2 parts in 100,000.

c. Springs and shallow wells contain a little more solids than lakes and rivers in the same region. The range may be from 4 parts to 70 parts in 100,000.

d. In deep wells the total solids may range from 15 parts to 1500 parts in 100,000. When they run above 100 parts they become rather mineral waters and are not very good for domestic purposes.

Hard and Soft Waters.—The substances which are most commonly found dissolved in water in considerable quantity are the carbonates of calcium and magnesium, which are held in solution by dissolved carbon dioxid. These give to water the property known as *hardness.* They unite with soap, forming a precipitate, and until they are completely removed soap has no cleansing effect and makes no lather. Water containing little or none of these salts is called *soft water.*

When hard water is boiled it loses a part of its hardness. The soluble hydrocarbonates of calcium and magnesium are decomposed with the formation of the insoluble carbonates which are precipitated:

$$CaH_2(CO_3)_2 = H_2O + CO_2 + CaCO_3.$$
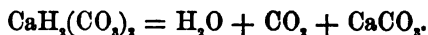
The hardness thus removed is called *temporary hardness.* The sulfates of calcium and magnesium are not precipitated by boiling, and these constitute the *permanent hardness.* The two together make up the *total hardness.*

Hardness is practically soap-destroying power and is measured in terms of calcium carbonate. Water has a hardness of 16 when it has a soap-destroying power equal to that of 16 parts of $CaCO_3$ in 100,000 parts of water.

It is the precipitation of these salts that causes the coating of cooking-vessels and steam-boilers when limestone water is used. A similar deposit takes place when water saturated with calcium carbonate is exposed to the air. The dissolved carbon dioxid escapes and the limestone is slowly deposited. It is thus that stalactites and stalagmites are formed in limestone caves. Each

drop of water as it falls from the roof leaves a portion of its calcium carbonate and presently there grows downward the pendent stem of stone called the *stalactite*. The drops falling to the floor deposit more solid matter and so another stem grows upward called the *stalagmite;* and in due time the two meet, making a column from floor to roof.

Potable Waters.—The water which is to be used for domestic purposes should be *sanitarily* pure. The dissolved gases, oxygen and carbon dioxid, give it sparkle and pleasant taste, and without them water is insipid and unwholesome. The mineral matters found in potable waters are generally healthful and are no doubt used to some extent as food for the body.

There are several sources of danger in natural waters, among which the following are the more important:

1. *Poisonous metals.* These are of very rare occurrence and are generally due to carelessness in handling the water.

2. *Organic matters.* There is usually not enough organic matter in solution in uncontaminated waters to have much physiological effect. It is dangerous mainly as it furnishes food for micro-organisms.

3. *Sewage and surface drainage.* These are dangerous in two ways. In the first place they interfere with digestion, produce diarrhœa, and render the system susceptible to disease. In the second place they are liable to contain disease germs, and sewage furnishes a fertile soil for their development.

4. *Living organisms.* All water which contains much organic matter will be found teeming with living organisms. Among these may be present the germs of various epidemic and contagious diseases.

In the analysis of drinking-water the chemist looks first for organic matter and chlorin, as these furnish the best evidence of contamination. Organic matter is necessary for the development of germs, and chlorin is always high in sewage. The presence of nitrites also makes water suspicious, because they are formed in the decomposition of organic matter.

Potable waters may be classified as follows:

Safe: 1. Deep-spring water.
      2. Deep-well water.
      3. Water from mountain lakes and streams.

Suspicious: 1. Shallow-spring water.

　　　　　　 2. Shallow-well water.

　　　　　　 3. Stored rain-water.

　　　　　　 4. Country surface-water.

Dangerous: 1. Water from shallow wells in cities and near barns and cesspools.

　　　　　　 2. Water of rivers and lakes which receive sewage.

Tests for Impurities in Drinking-water.—A few simple *tests* are here given. For details the student is referred to works on water analysis. Hard waters are not unwholesome, but are bad *for* washing purposes. A large excess of chlorids, sulfids, nitrites, ammonia, or organic matter makes a water suspicious.

1. *Calcium and Magnesium.*—*Hardness.*—Boil 200 cc. of the water vigorously for fifteen minutes. Calcium and magnesium present as carbonates are precipitated and settle to the bottom as a white powder. The sulfates remain in solution.

Make a soap solution by dissolving one part of Castile soap in 100 parts of dilute alcohol (1 pt. alcohol to 2 pts. water). Place 50 cc. of the water to be tested in an eight-ounce bottle and add the soap solution from a buret by littles, shaking vigorously after each addition. A permanent lather does not form until all the calcium and magnesium is precipitated. The number of cubic centimeters of the soap solution required to make a permanent lather, multiplied by two equals approximately the degrees of total hardness in parts of calcium carbonate in 100,000 parts of water. The permanent hardness is determined in the same way in the boiled water of the last paragraph.

2. *Chlorids.*— Add to the water a few drops of nitric acid, then a solution of silver nitrate. Chlorin is precipitated as white silver chlorid, which soon darkens in the light.

3. *Sulfids.*—If sulfids, especially hydrogen sulfid, are present, a brown or black precipitate will fall with the silver chlorid.

4. *Sulfates.*—Add a few drops of hydrochloric acid, then a solution of barium chlorid. A fine wh'te precipitate of barium sulfate indicates sulfates.

5. *Nitrites.*—Acidify 250 cc. of the water with acetic acid and distil. Add the first part of the distillate to potassium iodid starch solution which has been slightly acidified with sulfuric acid. If nitrites are present, the iodin is set free and the starch colored blue. The presence of even small quantities of nitrites is good evidence of sewage contamination.

6. *Ammonia.*—From 500-cc. of the water distil off 100 cc. and collect in two 50-cc. tubes. Add to each of the tubes 2 cc. of Nessler's solution. A yellow color indicates ammonia, and the depth of the color furnishes a

means of measuring its quantity. This test is very delicate and will detect 1 part of ammonia in 100 million parts of water.

7. *Organic Matter.*—To 200 cc. of the water add 1 cc. of sulfuric acid and then dilute solution of potassium permanganate (1 pt. to 250 pts. water) until there is a decided purple color. Let stand for a while or warm. If the color fades, organic matter is present and has been oxidized by the permanganate. Continue to add the solution until the color is permanent. The amount of the solution used is a measure of the organic matter present.

HYDROGEN PEROXID.

Formula H_2O_2. Molecular weight 34. Density 17. Specific gravity 1.45. Structural formula H—O—O—H.

Occurrence.—Because of its instability and inactivity, hydrogen peroxid occurs free to only a limited extent. Traces of it are found in the air and in snow, dew, and rain. The quantity is said to be greatest on bright days, sunlight being favorable to its formation.

History.—Hydrogen peroxid was first prepared in 1818 by Thénard, who called it oxygenated water.

Preparation.—Hydrogen peroxid is formed:

1. By the action of acids, especially hydrochloric, sulfuric, carbonic, fluosilicic, phosphoric, and tartaric, upon certain peroxids, as those of barium, calcium, potassium, and sodium. Some of the reactions are as follows:

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2 \quad \ldots \ldots \quad (1)$$
$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2 \quad \ldots \ldots \quad (2)$$
$$BaO_2 + CO_2 + H_2O = BaCO_3 + H_2O_2 \quad \ldots \ldots \quad (3)$$
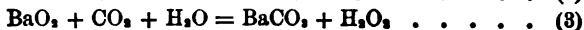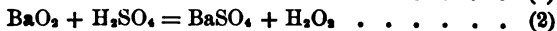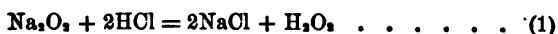
2. By the oxidation of water by nascent oxygen:

$$H_2O + O = H_2O_2 \quad \ldots \ldots \ldots \ldots \quad (4)$$

This action generally takes place in slow combustion. When ozone is prepared by the slow oxidation of phosphorus half immersed in water, the water is found to contain hydrogen peroxid. If a flame of hydrogen or carbon monoxid be allowed to play upon the surface of water whose temperature is kept below 20°, a small amount of the water is converted into hydrogen peroxid.

3. By the action of nascent hydrogen upon oxygen. If fragments of zinc or palladium hydrid be shaken with water in a flask containing air or oxygen, hydrogen peroxid is formed:

$$Zn + 2H_2O + O_2 = Zn(HO)_2 + H_2O_2 \quad \ldots \ldots \quad (5)$$
$$2Pd_2H + O_2 = 4Pd + H_2O_2 \quad \ldots \ldots \ldots \quad (6)$$
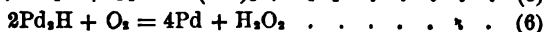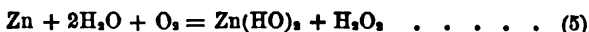
Zinc, copper, lead, and other metals act in the same way with dilute sulfuric acid. By the prolonged action of the metal a reverse action takes place and the hydrogen peroxid is decomposed. If air or oxygen be passed through water while it is being electrolyzed, hydrogen peroxid appears with the hydrogen at the negative electrode : $H_2 + O_2 = H_2O_2$.

Hydrogen peroxide may be conveniently prepared by either of the three reactions indicated under the first method.

1. Sodium peroxid is added to dilute well-cooled hydrochloric acid. The sodium chlorid which remains in solution does not interfere with the reactions of the hydrogen peroxid. (Equation 1.)

2. Moist barium peroxid (better the hydrated form, $BaO_2,8H_2O$) is added gradually to dilute sulphuric acid until it is nearly neutralized. The excess of acid is exactly removed by barium hydroxid solution and the liquid filtered off from the barium sulfate. (Equation 2.) For manufacturing purposes phosphoric acid is usually employed because the small amount of the acid remaining in the solution has a tendency to prevent the decomposition of the hydrogen peroxid.

3. A stream of carbon dioxid is passed through ice-cold water to which moist barium peroxid is added by littles from time to time. (Equation 3.) The precipitated barium carbonate is separated by filtration.

Physical Properties.—Hydrogen peroxid as obtained by any of the above methods is in dilute aqueous solution. It may be freed from the greater portion of its water by evaporation over strong sulfuric acid in vacuo, or by cooling to $0°$ and removing the frozen water. The strong solution is a colorless, odorless, syrupy liquid, with a harsh, bitter, astringent taste, and of specific gravity 1.452. At $-23°$ the 96 per cent solution becomes solid. If this solid be dropped into the solution cooled to $-10°$, splendid, transparent needle-shaped crystals of anhydrous H_2O_2 separate. It mixes with water in all proportions and goes over with the steam when very dilute solutions are distilled. Ether dissolves it readily and will remove it from its aqueous solution when the two are shaken together.

Chemical Properties.—Hydrogen peroxid is unstable because its formation from water is endothermic: $H_2O + O = H_2O_2 - 23,200$ cal. In concentrated solution it is unstable even at low temperatures $(-20°)$, and at $100°$ it decomposes with explosive violence into water and oxygen. In dilute solution it is more stable and can be kept for some time. It bleaches vegetable colors and whitens and blisters the skin.

Hydrogen peroxid is a vigorous oxidizing agent. It.converts selenium, arsenic, and chromium into their acids; sulfurous into sulfuric acid; sulfids into sulfates; and decomposes potassium iodid. It takes hydrogen from its compounds with sulfur, chlorin, bromin, and iodin, setting these elements free:

$$H_2O_2 + 2HI = 2H_2O + I_2.$$
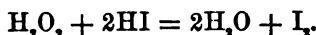
It is decomposed by nascent hydrogen. When a solution of hydrogen peroxid is electrolyzed no hydrogen is evolved, since it is oxidized as fast as it is set free, $H_2O_2 + H_2 = 2H_2O$. From the hydroxids of barium, strontium, and calcium the peroxids are separated, $Ba(HO)_2 + H_2O_2 = BaO_2 + 2H_2O$, and deposited in the crystalline hydrated form, $BaO_2,8H_2O$. The alkali peroxids are formed in the same way. They are soluble, but may be precipitated by adding alcohol and yield similar hydrated crystals.

With many substances, particularly oxidizing agents, hydrogen peroxid has a reducing action. Silver, mercury, and gold are separated from their oxids; the higher oxids of lead, chromium, and manganese are reduced to lower oxids; permanganates are converted into manganous compounds, and ozone to oxygen.

Hydrogen peroxid is decomposed by simple contact with many substances, especially when they are in a finely divided state. Such are charcoal, gold, platinum, silver, and mercury. The action is catalytic, but may be explained on the supposition that the metal is first oxidized and then the oxid reduced as follows:

$$Ag_2 + H_2O_2 = H_2O + Ag_2O$$
$$Ag_2O + H_2O_2 = H_2O + Ag_2 + O_2$$
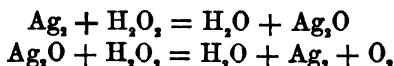
Illustrations.—Add hydrogen peroxid to solutions of litmus, potassium iodid starch, and potassium permanganate acidulated with sulfuric acid. The first and last are decolorized and the second is turned blue. The action of the first two is aided by the addition of a little ferrous sulfate.

Tests.—Hydrogen peroxid is recognized by its bleaching and oxidizing actions. A very convenient and characteristic test is made as follows: To the liquid to be tested add a dilute acidulated solution of potassium dichromate and a little ether, and shake. The ethereal layer which separates on standing will be colored blue if the peroxid is present. The test is quite delicate, as it will detect one part of hydrogen peroxid in 80,000 parts of water.

Uses.—Hydrogen peroxid is used in medicine and surgery as an antiseptic; in the laboratory as an oxidizing agent; in the arts as a bleaching agent for certain articles, as ivory, feathers, teeth, and hair; and for cleaning and restoring old and stained engravings and oil paintings. Paintings darken as they grow old because the white lead of the paint is gradually changed to black lead sulfid, PbS, by the traces of hydrogen sulfid found in the air. The H_2O_2 oxidizes the lead sulfid to white lead sulfate, $PbSO_4$, and restores the original color of the painting.

CHAPTER XX.

GROUP VIII B. THE HELIOIDS. THE NOBLE GASES.

Helium 4. Neon 20. Argon 40. Krypton 81. Xenon 128.

THE name *Noble Gases* has been given by Erdmann to the several rare and inactive elements which have recently been discovered. They are, with the exception of argon, found only in the smallest quantities, are almost wholly without chemical affinity, have no valence, form no compounds, and have monatomic molecules. They do not fit well into the periodic system. They may be given a separate group placed before the potassoids and called Group 0; or they may be arranged in Group VIII as VIII B, where they fall in reasonably well. Some of their physical properties are exhibited in the following table:

	Helium.	Neon.	Argon.	Krypton.	Xenon.
Atomic weight	4	20	40	81	128
Boiling-point		— 200°	— 186°	— 152°	— 109°
Melting-point			— 189°		
Critical temperature		— 205°	— 120°	— 58°	15°
Critical pressure		50.5	40 at.	54 at.	57 at.

HELIUM.

Symbol He. Atomic weight 4. Molecular weight 4. Density 2. Specific gravity 8.14. Valence 0.

Occurrence.—Helium occurs in the sun, in the earth's atmosphere in very small quantity, in nitrogen-holding springs, and more abundantly in the Scandinavian minerals of the rare earth-metals—uranium, thorium, yttrium, titanium, tantalum, and columbium. In these minerals it accompanies nitrogen, and is possibly in some sort of combination with the metals.

217

History.—In the year 1868 Janssen observed a prominent yellow line in the spectrum of the sun's chromosphere which could not be referred to any terrestrial element. He supposed it to be caused by an element peculiar to the sun and called it *helium* (Greek, *helios, the sun*). His observations were afterwards confirmed by Lockyer and Frankland. In 1882 Palmieri observed the same line when investigating lava from Vesuvius. In 1895 Ramsay and Cleve obtained the gas from the mineral cleveite.

Preparation.—Helium is most easily prepared from cleveite, a complex compound of uranium. The powdered mineral is gently heated to drive off water, carbon dioxid, and other gases. It is then mixed with an equal weight of potassium dichromate which has been previously melted and powdered, placed in a bulb, and heated to the melting-point of the dichromate, when the helium escapes with lively effervescence. The bulb is connected with a tube containing soda-lime and phosphoric oxid to remove traces of carbon dioxid and water, and then with the vessel which is to receive the gas, or with the Geissler tube, in which its spectrum is to be observed. The whole apparatus communicates with a mercury pump and is made vacuous before the operation. The gas is freed from nitrogen by sparking with oxygen, and from argon by diffusion.

Properties.—Helium is a colorless gas, only twice as heavy as hydrogen. It conducts electricity well and emits a bright light in the electric arc. It was liquefied by Onnes of Leyden in 1908, b. p. 4.3° absolute; not solid at 1 cm. pressure. Its spectrum consists of seven bright lines or bands: two red, one yellow, one green, and three blue or violet. One hundred volumes water dissolve 1.4 volumes at 20°.

In chemical properties helium resembles nitrogen, which it accompanies in a number of minerals and in the air. No compounds have been obtained and its valence is not known. The atmosphere contains about four parts in 100 millions (Ramsay).

NEON.

Symbol Ne.   Atomic weight 20 (19.86).   Molecular weight 20.   Density 10 (9.93).   Valence 0.

Occurrence and History.—Neon occurs along with argon in the air. It was discovered by Ramsay and Travers in 1898. The name is from the Greek, *neos, new.*

Preparation.—Neon is found in the argon prepared from air. If this argon is allowed to evaporate while being cooled by liquid air, the more volatile neon passes over first, together with the helium. It is separated from the latter by freezing it out with liquid hydrogen, the helium remaining gaseous.

Properties.—Neon is a colorless gas of vapor density 10. It liquefies and freezes below − 200°. Its critical temperature and pressure are about − 205° and 50 atmospheres. Like helium its molecule is monatomic, it is without valence and forms no compounds. Its spectrum is composed of many bright lines, mostly in the red and green. The air contains about one part in ten millions.

ARGON.

Symbol Ar. Atomic weight 40 (39.9). Density 20 (19.95). Molecular weight 40. Specific gravity 1.38. Boiling-point −186°. Melting-point −189.5.

Occurrence.—Argon is a constituent of the atmosphere of which it forms nearly one per cent (0.9). It is also found in the water of many springs, particularly geysers and mineral springs.

History.—As early as 1785 Cavendish noticed that a residue of about 0.6 per cent remained when the nitrogen and oxygen were removed from air. In 1894 Rayleigh discovered that nitrogen from the atmosphere was 0.5 per cent heavier than nitrogen prepared chemically. Rayleigh and Ramsay then prepared large quantities of this atmospheric residue and found it to be a gas different from nitrogen. They called it *argon* from the Greek, *argos, lazy.* They afterwards found that this residue was a mixture, and from it were separated later, by Ramsay and Travers, neon, krypton, and xenon.

Preparation.—For the preparation of argon, air, freed from moisture and carbon dioxid in the ordinary way and from oxygen by heated copper, is repeatedly drawn over heated magnesium whereby nitrogen is removed. Thus prepared, argon contains small quantities of the other noble gases. It is freed from helium and neon by freezing, and from krypton and xenon by diffusion.

Another method of obtaining argon, and the one by which it was first prepared, consists in passing electric sparks through a mixture of air and oxygen in a eudiometer tube. The nitrogen

and oxygen combine, and the nitric acid formed is absorbed by water. The excess of oxygen is removed with heated copper.

Properties.—Argon is a colorless gas of density 20, atomic and molecular weight 40, and has but one atom in the molecule. It becomes liquid and solid at low temperatures, boils at −186° and melts at −189.5°. Its critical temperature and pressure are −120° and 40 atmospheres. It is slightly soluble, 4 parts to 100, and is therefore found in terrestrial waters.

The spectrum of argon consists of a multitude of lines and bands which vary in brightness with the pressure. Under slight pressure and weak current the red lines are most prominent; with strong current and a little higher pressure the blue lines predominate; and with still higher pressure, 100 to 200 mm., the green lines are the brightest.

Chemically, argon is like the other noble gases, being without valence and forming no compounds.

KRYPTON.

Symbol Kr. Atomic weight 81.8. Density 40.9. Molecular weight 81.8. Valence 0.

Occurrence.—Krypton occurs in the atmosphere and is always a constituent of argon prepared from air. Air contains about one part of krypton in 20,000,000 parts.

History.—Krypton was discovered by Ramsay and Travers in 1898 in atmospheric argon. The name is from the Greek, *kruptein*, to *conceal*.

Preparation.—Krypton is separated from argon by fractional distillation.

Properties.—Krypton has properties very similar to those of argon. It is heavier and more easily liquefied and solidified. It boils at −152° and its critical pressure and temperature are 53° and 54 atmospheres. Its spectrum consists of three lines in the green, six in the red, and about a dozen in and beyond the blue.

XENON.

Symbol Xe. Atomic weight 128. Density 64. Molecular weight 128. Valence 0.

Occurrence and History.—Xenon occurs along with argon and krypton in the atmosphere, but only in exceeding small quantities

—one part to 150,000,000. It was discovered by Ramsay and Travers at the same time with krypton, 1898. The name is from the Greek, *xenos*, a *guest*, as accompanying argon and krypton in the air.

Properties.—Xenon has properties resembling those of argon and krypton. It is without valence or chemical activity and no compounds are known. It boils at $-109°$, and its critical temperature and pressure are $15°$ and 57 atmospheres.

CHAPTER XXI.

GROUP VII B. THE CHLOROIDS. CHLORIN GROUP.

Fluorin 19. Chlorin 35.45. Bromin 80. Iodin 127. Thulium 171.

FLUORIN, chlorin, bromin, and iodin constitute a group of closely allied elements called *halogens* (Greek, *salt-makers*), because all their binary compounds with the alkali metals (Group I A), called *haloid salts*, have a close resemblance to common salt, NaCl. The rare element thulium is provisionally placed in this group.

Taking these elements in order, we find a gradual increase in atomic weight and a corresponding decrease in chemical activity. Fluorin and chlorin are gases, bromin is a liquid, and iodin a solid. Fluorin is chemically most active, and iodin least. We have in this group a fine illustration of the group gradation of properties, as will appear by the following table:

	Fluorin.	Chlorin.	Bromin.	Iodin.
Atomic weight..............	19	35.4	80	127
Specific gravity of liquid......	....	1.33	3.18	4.97
Melting-point................	−187°	− 102°	− 7°	127°
Boiling-point................	−233°	− 33.6	63°	200°
Color......................	none	yellow	brown	black
Heat of union with H........	....	22,000 cal.	8,440 cal.	−6,200 cal.
Haloid acids................	HF	HCl	HBr	HI
Acids decompose at	not at all	1500°	800°	180°

The halogens are chemically very active, uniting directly with nearly all the elements and entering as a constituent an immense number of compounds, organic as well as inorganic. Their compounds with the metals are called *halids*.

FLUORIN.

8ymbol F.   Valence I and III.   Atomic weight 19.   Density 19.

Occurrence.—On account of its great chemical activity fluorin does not occur free in nature. Its principal native compound is calcium fluoride, CaF_2, called *fluorite*, or *fluorspar*. It is a constituent of various minerals, such as cryolite, topaz, fluor-apatite, wavelite, etc. It occurs in sea-water and some mineral springs. It has been found in the enamel of the teeth, in the bones, blood, brain, and milk, and in the ashes of plants.

History.—While fluorin compounds are quite common, the element is so active that its preparation is very difficult. In the year 1886 Moissan succeeded in isolating it by electrolysis of hydrogen fluorid in the presence of potassium fluorid. Its name is from the Latin, *fluo, I flow*, and fluorite was so called because it was used as a flux in working certain metals.

Preparation.—Moissan prepared fluorin by passing the electric current through a solution of acid potassium fluorid, HF,KF, in anhydrous hydrofluoric acid. The fluorin was set free at the positive electrode, while hydrogen was evolved at the negative. It cannot be obtained from hydrofluoric acid because the fluorin decomposes the water.

The apparatus employed is a U tube made of an alloy of platinum and iridium, with electrodes of the same material. The liquid hydrofluoric acid 'is introduced, and then one fourth as much acid potassium fluorid added. Since the liquid hydrofluoric acid used is very volatile, the apparatus must be cooled to a low temperature. For this purpose it is immersed in methyl chlorid, by the evaporation of which the temperature can be kept at — 40°.

Fluorin has also been obtained by Brauner by heating to 250° hydrogen potassium fluoplumbate, $3KF,HF,PbF_4$.

Physical Properties.—Fluorin is a gas, colorless or possibly of a pale yellow color. The odor is irritating and very characteristic, resembling that of chlorin and the oxids of chlorin. On account of the great difficulty of handling it, its physical constants have not been fully determined. Its critical temperature and pressure are — 121° and 50.6 atmospheres. It liquefies at — 187° and solidi-

fies at −233°. Its density has been approximately determined and is such as to indicate the molecular formula F_2.

Chemical Properties.—Fluorin is the most active of the chemical elements. It unites with all the other elements, even gold and platinum, and the action is in many cases intensely energetic. It unites explosively with hydrogen, bromin, and iodin. Sulfur, phosphorus, silicon, and finely divided metals take fire and burn with vigor in it. It decomposes organic matters and inorganic compounds generally except the fluorids. Its principal compounds are the fluorids. No oxids nor ternary acids have been prepared, but it forms fluo-acids and fluo-salts.

Physiological Properties.—Fluorin is irritating to the respiratory organs and dangerous in the extreme. It should not be breathed even in the smallest quantity.

CHLORIN.

Symbol Cl. Valence I, also III, V, VII, and apparently II and IV. Atomic weight 35.45. Density 35.45. Molecular formula Cl_2. Molecular weight 70.9. Specific gravity 2.45. Liter weighs 3.18 grams.

Occurrence.—Chlorin is chemically too active to occur free in nature. Its most abundant compound is sodium chlorid, NaCl, or common salt, which is universally distributed over the earth, being found in all soils and waters, and in the bodies of plants and animals. It is the principal dissolved substance in sea-water and salt springs, and also occurs in beds of considerable extent as rock salt. Other compounds are potassium chlorid, KCl, found in soils, waters, and plants; magnesium chlorid, $MgCl_2$, found in waters and soils, and chlorids of iron, lead, silver, and copper, found in nature in small quantities.

History.—Chlorin was first prepared by Scheele in 1774, who thought it a compound. Berthollet, in 1785, studied its properties and called it *oxymuriatic acid*, supposing it to contain oxygen. Its elementary character was suggested by Gay-Lussac and Thénard in 1809 and satisfactorily proved by Davy in 1810. Its name, which means *greenish-yellow*, was given it by Davy.

Preparation.—Chlorin is obtained from its compounds in many ways:

1. By action of heat or electricity upon chlorids:

$$PtCl_4 = PtCl_2 + Cl_2 \quad \ldots \ldots \ldots \quad (1)$$

$$LHCl = H_x + Cl_x \quad \ldots \ldots \ldots \ldots \quad (2)$$

2. By the action of acids upon alkaline hypochlorites:

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2 \quad \ldots \ldots \quad (3)$$
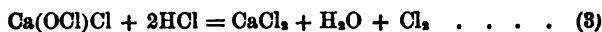
3. By the action of oxygen or oxidizing agents upon hydrochloric acid or chlorids, the oxygen taking the hydrogen or the metal and setting the chlorin free:

$$2MgCl_2 + O_2 = 2MgO + 2Cl_2 \quad \ldots \ldots \ldots \quad (4)$$

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2 \quad \ldots \ldots \quad (5)$$

$$2NaCl + 2H_2SO_4 + MnO_2 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2 \quad . \quad (6)$$

$$12HCl + 4KClO_3 = 4KCl + 6H_2O + 3ClO_2 + 9Cl \quad \ldots \quad (7)$$
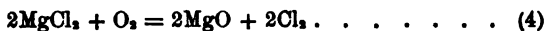
Chlorin is most conveniently prepared from manganese dioxid and hydrochloric acid. (Equation 5.) The materials are gently warmed in a flask furnished with safety- and delivery-tubes. The gas is collected by displacement of air, or over brine or warm water, but not over mercury. If pure dry chlorin is desired, it is passed through a water wash-bottle to remove hydrochloric acid and through sulfuric acid to remove moisture. Chlorin should always be prepared under a hood or where there is a draft to carry the fumes away.

For bleaching and distinfecting purposes chlorin is obtained from chlorid of lime. (Equation 3.)

Chlorin is prepared on a large scale for manufacturing purposes by the electrolysis of sodium or potassium chlorid in solution, the metals separating at the cathode as hydroxids while the chlorin is liberated at the anode.

In another method the chlorin is obtained by the action of hydrochloric acid upon native manganese dioxid, pyrolusite (Equation 5). The manganous chlorid is recovered by the *Weldon process*. The still liquor containing the manganous chlorid is treated with lime and then with air and steam, whereby calcium manganite is formed:

$$MnCl_2 + 2Ca(HO)_2 + O = CaMnO_3 + CaCl_2 + 2H_2O.$$
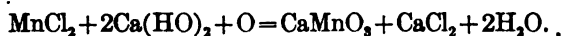
This is returned to the still where with hydrochloric acid it yields chlorin:

$$CaMnO_3 + 6HCl = CaCl_2 + MnCl_2 + 3H_2O + Cl_2.$$
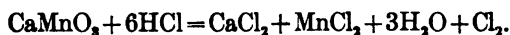
The *Deacon process,* another manufacturing method, consists in decomposing hydrochloric acid with oxygen in the presence of cuprous chlorid. Fragments of brick are impregnated with the chlorid and heated to redness in a tube while a mixture of air and the acid is passed over them. The cuprous chlorid acts as a carrier of oxygen and is used continuously. The reactions are supposed to be represented by the following equations:

$$Cu_2Cl_2 + O = Cu_2OCl_2 \text{ (cuprous oxychlorid).}$$
$$Cu_2OCl_2 + 2HCl = H_2O + 2CuCl_2 \text{ (cupric chlorid).}$$
$$2CuCl_2 = Cu_2Cl_2 + Cl_2.$$
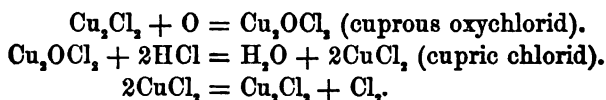
Physical Properties.—Chlorin is a yellowish-green gas with a sharp, suffocating odor and an astringent taste. Its atomic weight is 35.45, its specific gravity is 2.46, and a liter weighs 3.18 grams. Its vapor density at 200° is equal to its atomic weight and therefore its molecule contains two atoms.. Below 200° the density increases, showing that there is molecular condensation, while above that temperature the density diminishes, showing partial dissociation.

Under the atmospheric pressure chlorin becomes a liquid at — 34°. At 0° the pressure required is 6 atmospheres and at 15° 10 atmospheres. The critical temperature of chlorin is 146° and its critical pressure is 94 atmospheres. Liquid chlorin has a golden-yellow color, does not mix with water, has a low refractive index, and is a non-conductor of electricity. Its specific gravity is 1.56, it boils at — 33.6°, and freezes at — 102° to a yellow crystalline mass.

Chlorin is quite soluble, one volume of water dissolving 2.6 volumes at 10° and 2 volumes at 21°. The solution has the color, odor, and general chemical properties of the gas and is called *chlorin water.* It readily gives up the chlorin when exposed to the air or when heated. When exposed to light the chlorin slowly unites with the hydrogen of the water, setting oxygen free: $H_2O + Cl_2 = 2HCl + O.$

Below 10° water dissolves a larger quantity of chlorin, and pale-green, scale-like crystals of *chlorin hydrate,* $Cl_2, 10H_2O$, are formed. This compound is unstable and soon decomposes into chlorin and chlorin water. If the crystals be quickly dried with blotting-paper and then sealed up in a glass tube, they remain

unchanged and may be heated even to 38° before separation takes place.   At this temperature two layers are formed in the tube, one of chlorin water and the other of liquid chlorin.

Illustrations.—Chlorin water is made by allowing the gas to bubble slowly through water in a bottle.

Chlorin hydrate is obtained by passing the gas into water whose temperature is slightly above 0°.   The crystals are dried with blotting-paper and preserved in sealed glass tubes.

Liquid chlorin is most easily prepared from the hydrate.   This is placed in one end of a strong bent tube and the tube sealed.   On being gently warmed the hydrate disso-ciates and the chlorin is liquefied by the pressure within the tube.   On immersing the empty limb of the tube in a freezing mixture the liquid chlorin distils over and is thus separated from the chlorin water.
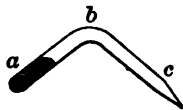
Fig. 54.

Chemical Properties.—The chemical activity of chlorin is very great.   It unites directly with all the elements except carbon, nitrogen, and oxygen, and the chlorids of these are easily formed by chemical processes.   It is an energetic supporter of combustion. Both metals and non-metals take fire in it either spontaneously or at a moderate temperature and burn with great vigor, forming chlorids.   So great is its affinity for most of these elements that it is even able to wrest them from their combinations, and thus there are few substances which are free from its attacks.   It has but little attraction for oxygen and nitrogen and hence it does not burn in the air.   It displaces bromin and iodin from their com-pounds and is itself displaced by fluorin.

The affinity of chlorin for hydrogen is specially marked.   The mixed gases combine with explosive violence; compounds contain-ing hydrogen are generally decomposed by it.   It acts upon or-ganic matters, uniting directly to them or displacing hydrogen or taking hydrogen from them and setting carbon free.   It is indirectly a powerful oxidizing agent.   It takes hydrogen from water, and the nascent oxygen set free attacks any oxidizable matter present.   It is in this way a bleaching agent and a dis-infectant.   Mineral colors are not destroyed unless they admit of further oxidation, and dark tints due to carbon, such as printers' ink, are not affected by it.   It raises many oxids to peroxids and converts sulfur into sulfuric acid.

Illustrations.—The chemical activity of chlorin and its power of support-ing.combustion are shown in various ways :

1. Lower a jet of burning hydrogen in a jar of chlorin. It continues to burn with a white flame: $H + Cl = HCl$.

2. Lower a bit of phosphorus on a combustion-spoon in a jar of chlorin. It burns vividly: $P_4 + 6Cl_2 = 4PCl_3$.

3. Drop powdered antimony into chlorin: $Sb + Cl_3 = SbCl_3$.

4. Lower a lighted candle in chlorin. It continues to burn, but with a smoky flame, carbon being set free.

5. Dissolve gold leaf in chlorin water in a test-tube.

The action of chlorin upon water may be shown by inverting a jar of chlorin water and exposing it to sunlight. The oxygen collects at the top of the jar: $H_2O + Cl = 2HCl + O$.

The action of chlorin upon organic compounds is shown as follows:

1. Fill a jar inverted over water half full of chlorin, then add rapidly an equal volume of ethylene. Oily drops of ethylene chlorid sink to the bottom of the vessel: $C_2H_4 + Cl_2 = CH_4Cl_2$.

2. Fill a jar over salt water with equal volumes of marsh-gas and chlorin and expose to sunlight. The hydrochloric acid produced is ab-sorbed by the water and methyl chlorid remains:

$$CH_4 + Cl_2 = HCl + CH_3Cl.$$
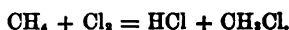
3. A piece of tissue-paper moistened with warm oil of turpentine takes fire in chlorin and burns with a smoky flame:

$$C_{10}H_{16} + 16Cl = 16\ HCl + 10C.$$

To show the bleaching and disinfecting action of chlorin :

1. Add chlorin water to a solution of indigo or litmus. The blue color disappears immediately.

2. Suspend pieces of moistened calico in a jar of weak chlorin. In a little while the colors will be discharged.

3. To a jar containing hydrogen sulfid add chlorin water. The odor of the hydrogen sulfid disappears.

Physiological Properties.—Chlorin is poisonous and dangerous. A single inspiration of the pure gas would no doubt produce death. An atmosphere containing even small quantities induces in a little while headache and languor. Chlorin should therefore be handled with great care.

Uses.—Chlorin is used in bleaching and disinfecting, in the manufacture of chlorid of lime, in the extraction of gold from its ores, and as a reagent in chemical laboratories. Liquid chlorin is transported in lead-lined iron bottles for use where it is not con-venient to prepare chlorin.

Tests.—Free chlorin is known by its color, odor, and general chemical properties. In solution it is recognized by its bleaching action, its power of dissolving gold, and its producing a blue color in solutions of potassium iodid and starch. The general reagent for chlorin, both free and combined, is silver nitrate, from which it precipitates silver chlorid, a white substance insoluble in acids but soluble in ammonia.

BROMIN.

Symbol Br. Valence I, also V and VII. Atomic weight 80. Density 80. Molecular formula Br_2. Molecular weight 160. Specific gravity 3.187. Liter of vapor weighs 7.146 grams.

Occurrence.—Bromin does not occur free. Its principal native compounds are the bromids of magnesium, calcium, sodium, and potassium. These are widely distributed in nature, but always in small quantities. They are found in sea-salt and mineral waters and are commonly associated with the corresponding chlorids. Certain silver ores from Chili and Mexico contain silver bromid. Bromin has also been found in seaweeds and some marine animals.

History.—Bromin was discovered by Balard in 1826. He obtained it from the bittern or mother-liquor that remained after the common salt had crystallized out of concentrated sea-water. He gave it its name from the Greek word which means *stench*.

The larger part of the bromin of commerce comes from the salt-wells of the United States, particularly West Virginia, Michigan, and Ohio. In Europe the chief source of supply is the potassium-chlorid mines of Stassfurt, Germany.

Preparation.—Bromin is obtained by reactions similar to those which yield free chlorin. The most important are

1. By the action of chlorin upon bromids :

$$NaBr + Cl = NaCl + Br \quad \dots \dots \dots \quad (1)$$

2. By the joint action of manganese dioxid and sulfuric acid upon bromids:

$$2KBr + 2H_2SO_4 + MnO_2 = K_2SO_4 + MnSO_4 + 2H_2O + Br_2 \quad . \quad (^{\cdot}$$
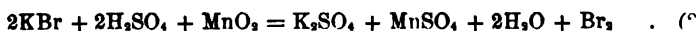
There are two methods of preparing bromin on a large scale, in both of which the bittern of the salt works is used. This contains bromids and chlorids of magnesium, sodium, and potassium.

In the first method the mother-liquor is mixed with manganese dioxid and sulfuric acid and heated in stone stills. The chlorin set free from the chlorids acts upon the bromids, setting the bromin free, which distils over and is retained in condensers. The reactions are as follows:

$$MgCl_2 + MnO_2 + 2H_2SO_4 = MnSO_4 + MgSO_4 + 2H_2O + Cl_2 \quad (3)$$
$$MgBr_2 + Cl_2 = MgCl_2 + Br_2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$
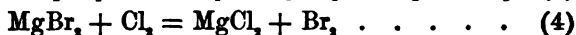
Some of the bromin is also liberated according to equation (2).

In the second method the chlorin is generated in a separate vessel and brought in contact with the mother-liquor as it descends through a tower. The bromin is carried away by a current of steam and collected in condensers.

Illustrations.—Pass chlorin gas through (or add chlorin water to) a solution of potassium or sodium bromid. A brown color appears indicating the liberation of bromin. (Equation 1.) Add a little ether and shake. The ether dissolves the bromin.
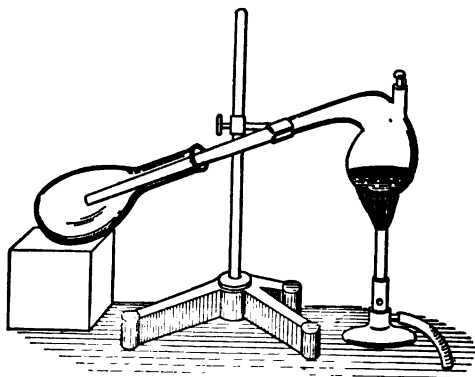
Fig. 55.

To prepare bromin according to reaction 2 above, place 2 grams each of potassium bromid, manganese dioxid, and sulfuric acid in a small retort whose neck passes into a well-cooled receiver containing a small quantity of water. Upon the application of a gentle heat the bromin distils over and collects under the water in the receiver. The water is colored by dissolved bromin.

Physical Properties.—Bromin is a heavy, mobile, opaque, reddish-brown liquid, with a penetrating chlorin-like odor and a specific gravity at 0° of 3.188. It boils at 59°, yielding dark-brown vapors which are more than five times as heavy as air. It

is very volatile, evaporating rapidly at the ordinary temperature, and can only be kept in well-stoppered bottles. The vapor density corresponds to the formula Br_2, but as the temperature rises, dissociation takes place and is complete at 1200°. It freezes at $-$ 7° to a brown, crystalline solid. Bromin is the only non-metal which is liquid at the ordinary temperature.

Bromin forms with water a yellow solution called *bromin water*, which possesses all the properties of the liquid. One hundred volumes of water dissolve at 5° 3.6 volumes of bromin, at 10° 3.33 volumes, at 20° 3.2 volumes, and at 30° 3.1 volumes. It is more soluble in alcohol, ether, chloroform, and carbon disulfid.

When bromin water is cooled to 0° *bromin hydrate*, $Br_2, 10H_2O$, separates as a red crystalline solid which decomposes at 15°.

Chemical Properties.—Chemically bromin resembles chlorin very closely, but its activity is less. Its affinity is especially strong for hydrogen and the metals, but it does not unite with oxygen. It displaces iodin and is itself displaced by chlorin. It acts on organic compounds just as chlorin does. Like chlorin it is an oxidizing agent because of its affinity for hydrogen. It bleaches faintly and colors starch yellow. The aqueous solution remains unchanged in the dark, but in sunlight HBr is formed and oxygen set free: $Br_2 + H_2O = 2HBr + O$.

Illustrations.—The properties of bromin may be illustrated by a series of experiments similar to those used with chlorin. The action of certain metals, as potassium and antimony, upon liquid bromin is very violent and the experimenter should use small quantities and be well on his guard. The bromin is best taken from the bottle with a bulb dropper.

To show its volatility place a single drop in a small flask.

To show its solubility add a drop to a test-tube of water and shake.

To show its displacement by chlorin and its action on starch add chlorin water to potassium bromid starch solution: $KBr + Cl = KCl + Br$.

To show its action upon metals place a few drops in a test-tube and add carefully a small fragment of antimony: $Sb + Br_3 = SbBr_3$.

Physiological Properties.—Bromin is a corrosive poison. Its odor is unpleasant and suffocating. It is irritating to the mucous membrane of the throat, nose, and eyes. The liquid burns the skin and makes sores which heal with difficulty.

Uses.—Bromin is used in laboratories for various purposes, particularly as an oxidizing agent. It is used in the manufacture

of anilin colors and other organic compounds.   The bromids are used in medicine and in photography.

Tests.—Free bromin is recognized by its odor and its effect upon starch solution.   Bromids give with silver nitrate, $AgNO_3$, a precipitate of silver bromid: $AgNO_3 + HBr = HNO_3 + AgBr$.

IODIN.

Symbol I.   Valence I, also III, V, and VII.   Atomic weight 127. Density 127.   Molecular formula I_2.   Molecular weight 254.   Specific gravity 4.95.   Liter of the vapor weighs 11.334 grams.

Occurrence.—Iodin does not occur free.   Its principal compounds are the iodids and iodates of potassium, sodium, magnesium, and calcium.   These are widely distributed in small quantities.   They are found in sea-water, mineral springs, and marine plants and animals.

Until recent years the principal source of the iodin of commerce was the ash of seaweeds found on the coasts of Ireland, Scotland, and France.   Now it is mostly obtained from the sodium iodate, $NaIO_3$, and sodium iodid, NaI, which are found in small quantities in the sodium nitrate which comes from Chili and Peru.

History.—Iodin was discovered by Courtois, of Paris, in 1812, in the mother-liquors obtained in the preparation of sodium salts from kelp or burnt seaweeds.   Its elementary character was established by Gay-Lussac in 1815.   Its name is Greek and means *violet*, referring to the color of its vapor.

Preparation.—Iodin may be prepared from the iodids by the action of chlorin:

$$KI + Cl = KCl + I \quad . \quad . \quad . \quad . \quad . \quad (1)$$
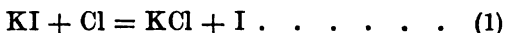
Or as in the case of chlorin and bromin by the action of manganese dioxid and sulfuric acid upon iodids:

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2 \quad (2)$$
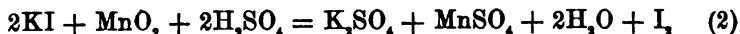
Pure iodin is best prepared by heating dry potassium iodid in excess with dry potassium dichromate:

$$5K_2Cr_2O_7 + 6KI = 8K_2CrO_4 + Cr_2O_3 + 6I.$$

Illustrations.—Pour a little sulfuric acid on a few crystals of potassium iodid in a test-tube.   Iodin is set free and at the same time fumes of hydrogen iodid are seen.

Place in a small retort a mixture of equal parts of potassium iodid and

manganese dioxid and cover with sulfuric acid. On the application of heat the iodin distils over and condenses in the tube of the retort or in a condenser.

Physical Properties.—Iodin is a dark bluish gray, shining, solid, crystallizing in rhombic prisms or in scales which have a specific gravity of 4.95. Thin leaves transmit red light. It has a peculiar odor resembling that of chlorin and bromin, and a taste which is characteristically sharp and astringent. It melts at 116° to a dark-brown liquid, and boils at about 180°, giving a heavy dark violet vapor. Its heat of fusion is 11.7 calories and its heat of vaporization is 24 calories. It is volatile at the ordinary temperature and may be sublimed without melting. Its vapor density up to 700° corresponds to the formula I_2. Above this temperature dissociation takes place and at 1500° amounts to about 75 per cent. The specific heat of solid iodin is 0.054, liquid 0.109.

Iodin is but slightly soluble in water, one part requiring 5524 parts of water at 10°. It is freely soluble, with brown color, in alcohol, ether, and aqueous solution of potassium iodid. The solution in chloroform, carbon disulfid, and other liquid hydrocarbons is violet. The tincture of iodin of the drug-store is a solution of one part of potassium iodid and two parts of iodin in 64 parts of alcohol.

Illustrations.—Note the color, odor, and taste of iodin. Place a crystal in a tube and gently warm it. Violet vapors fill the tube and crystals form on the wall.

Add to the tube a few cubic centimeters of alcohol and form solution.

Chemical Properties.—Chemically iodin is similar to chlorin and bromin, but less active. It is replaced from its compounds by both these elements, as well as by fluorin:

$$KI + Br = KBr + I \quad . \quad (3) \qquad NaI + Cl = NaCl + I \quad . \quad (4)$$

It unites directly with phosphorus, antimony, mercury, zinc, iron, potassium, and other metals. Its action with potassium and phosphorus is specially violent.

$$K + I = KI \quad . \quad (5) \qquad P + I_3 = PI_3 \quad . \quad (6)$$

It forms but one oxid, I_2O_5. The hydrogen compound HI must be formed indirectly and is quite unstable.

It acts as an oxidizer in the presence of water, but not very strongly.   It converts sulfurous into sulfuric acid:

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

It colors starch blue, and this property affords a very delicate test for iodin.   The nature of this blue solution is not known.   It loses its color at 80°, but the color returns on cooling.   The color is destroyed by boiling.   Solutions of iodin are decolorized by potassium hydroxid, the iodid and iodate being formed:

$$6I + 6KHO = 5KI + KIO_3 + 3H_2O \quad \cdot \quad \cdot \quad \cdot \quad (8)$$
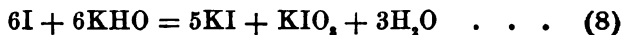
Nitric acid oxidizes it to iodic acid, HIO_3.

Illustrations.—Lay a crystal of iodin on a small piece of phosphorus. The heat of the reaction sets the phosphorus on fire.

Mix in a tube water, iodin, and filings of iron or zinc and note the action.

Dissolve in a jar of water a small crystal of potassium iodid and a little starch paste, then add a few drops of chlorin water.   The iodin set free colors the starch blue.   To get the best results the solution must not be too strong.   This is the characteristic test for iodin and is so delicate that it will detect 1 part of iodin in 400,000 parts of water.

Add potassium hydroxid to a solution of iodin.   The color disappears.

Physiological Properties.—Iodin acts upon the mucous membranes, but less actively than the other halogens.   It colors the skin brown and acts as an absorbent and counter-irritant.

Uses.—Iodin is used in chemical laboratories, in medicine, in the manufacture of anilin colors, and to a limited extent in photography.   Nearly a million pounds are consumed annually.

Tests.—Iodin is recognized by the blue color it gives to starch and the purple color of its solution in carbon disulfid.   The iodids give characteristic precipitates with salts of lead and mercury.

Illustrations.—In three jars containing dilute solutions of potassium iodid add solutions respectively of lead acetate, mercurous nitrate, and mercuric chlorid.   Precipitates are formed in the first of yellow lead iodid, PbI_2 ; in the second of yellowish-green mercurous iodid, Hg_2I_2 ; in the third of red mercuric iodid, HgI_2.

THULIUM.

Symbol Tu.   Atomic weight 171.   Valence I and III (?).

In 1879 Cleve discovered a new earth in a sample of gadolinite.   He named it *thulia*, from Thule, the ancient name of Scandinavia.   The element has not been sufficiently studied to justify its description here.

CHAPTER XXII.

HALOID ACIDS AND OTHER COMPOUNDS.

HALOID ACIDS.

HYDROGEN forms one compound with each of the halogens. These are all colorless gases and present a regular gradation of properties. Hydrogen fluorid is the most stable and yet at the same time the most active, because of the activity of fluorin. Hydrogen iodid is the least stable and at the same time the least active.

These compounds all dissolve in water to acid solutions, but do not seem to form definite hydrates. In writing their formulas the water is not included, and so they are called binary acids. They undergo dissociation in the presence of water, and the aqueous acid always contains hydrogen ions and halogen ions. They act with bases like other acids, yielding binary salts; as,

$$HCl + Na = NaCl + H, \quad HBr + KHO = KBr + H_2O.$$
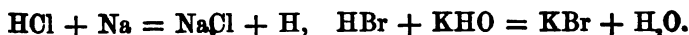
The acids and a few typical halids are as follows:

HF	KF	NaF	MgF_2	CaF_2	AlF_3	SiF_4
HCl	KCl	NaCl	$MgCl_2$	$CaCl_2$	$AlCl_3$	$SiCl_4$
HBr	KBr	NaBr	$MgBr_2$	$CaBr_2$	$AlBr_3$	$SiBr_4$
HI	KI	NaI	MgI_2	CaI_2	AlI_3	SiI_4

HYDROGEN FLUORID. HYDROFLUORIC ACID.

Formula HF and H_2F_2. Structure H—F and H—F=F—H. Molecular weight 40 and 20. Density 20 and 10. Specific gravity of liquid 0.99.

Occurrence and History.—Hydrogen fluorid does not exist free. It was discovered by Scheele in 1771.

Preparation—Hydrogen fluorid is prepared

1. By heating the double fluorid of hydrogen and potassium :

$$HF,KF = KF + HF \quad \ldots \ldots \ldots \ldots \text{(1)}$$

2. By the action of hydrogen upon silver fluoride :

$$AgF + H = Ag + HF \quad \ldots \ldots \ldots \text{(2)}$$

8. By the action of sulfuric acid upon fluorids :

$$H_2SO_4 + CaF_2 = CaSO_4 + 2HF \quad \ldots \ldots \text{(3)}$$
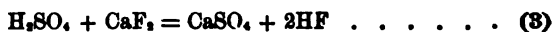
By the first two methods perfectly dry and pure hydrogen fluorid is obtained. The third method is most convenient and the one usually employed, though the gas thus obtained is not dry. Finely pulverized fluorspar, CaF_2, is heated with sulfuric acid in a lead or platinum retort. The gas is condensed in a U tube immersed in a freezing mixture, or is conducted into water contained in lead or platinum vessels. As the gas is a deadly poison it must be handled with extreme caution.

Physical Properties.—Anhydrous hydrogen fluorid is a colorless, fuming liquid of specific gravity 0.99 at 12°. It boils at 19° and solidifies at —93°. Its vapor density at 32° corresponds to the formula H_2F_2, but as the temperature rises dissociation takes place, until at 88° the density is 10, which gives it the formula HF.

Hydrogen fluorid dissolves readily in water, forming the solution called *hydrofluoric acid*, which when saturated has a specific gravity of 1.25. At 120° an acid distils over having a specific gravity of 1.15 and containing 35.7 per cent of HF.

Chemical Properties.—Hydrofluoric acid is one of the most active of all substances. It dissolves all the metals to form *fluorids* except gold, platinum, and lead. It decomposes the most stable oxids, the carbonates and the silicates. It readily dissolves glass and cannot be kept in ordinary bottles. It unites with the silicon of the glass to form silicon fluorid, SiF_4. It is preserved in vessels of lead, platinum, or gutta percha. Laboratory supplies are usually kept in bottles made of ceresine, a kind of wax.

The anhydrous liquid possesses properties somewhat different from those of the solution. It seems not to be able to start an action without the help of moisture. Glass and some of the metals are free from its attacks, but the presence of the smallest amount of moisture causes the action to begin.

The acid gives rise to three kinds of salts called *fluorids, acid fluorids,* and *double fluorids.* Examples are calcium fluorid, CaF_2, hydrogen potassium fluorid, HF,KF, and sodium aluminum fluorid, Na_3F_3,AlF_3. These compounds are explained by the double molecule of hydrogen fluorid, H_2F_2. There may be a simple molecular union, or the fluorin may have a valence three. On the latter supposition the second formula would have this structure: H—F=F—K, and the third would be written thus:

$$Al\begin{cases} F=F—Na \\ F=F—Na \\ F=F—Na \end{cases}$$
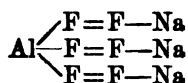
Illustrations.—The formation of hydrogen fluorid and the etching of glass may be shown as follows : A gram of powdered calcium fluorid (fluorspar) is placed in a dish of lead or iron and enough strong sulfuric acid added to make a paste. A piece of window-glass is covered with a coating of wax by the aid of heat, and designs drawn upon it with a sharp point cutting through the wax. The glass is then laid wax down upon the dish and a gentle heat applied below until fumes of the gas are seen. In a little while the lines will be found to be etched in the glass. The wax may be melted and removed with a rag or scraped away with a knife.
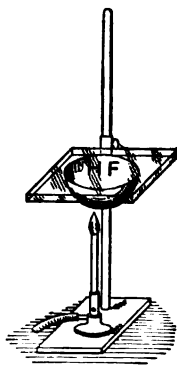
Fig. 56.

Tests and Uses.—Hydrofluoric acid is recognized by its etching properties. It is largely used for graduating glass apparatus and ornamenting glassware.

Fluorid Ion.—The dissociation of hydrogen fluorid is much less than that of the other haloid acids, amounting to only about 3 per cent in the normal solution. The activity of the acid and of all soluble fluorids is mainly due to the fluorid ion F', which is possibly the most active of all ions. This ion is colorless and univalent and always negative. Its heat of formation from molecular fluorin is 53,800 calories. Fluorin also forms complex ions as in the fluoacids and fluosalts.

HYDROGEN CHLORID. HYDROCHLORIC ACID.. MURIATIC ACID.

Formula HCl. Molecular weight 36.45. Density 18.2. Specific gravity 1.26. Liter weighs 1.63 grams.

Occurrence.—This, the only compound of hydrogen and chlorin, scarcely occurs native except in the exhalations of active volcanoes

(Vesuvius and Hecla) and in some rivers in volcanic regions, as in South America.   It is a constituent of the gastric juice of vertebrate animals.

History.—Aqua regia, a mixture of hydrochloric and nitric acids. was known to the Arabian alchemists.   Basil Valentine in the fifteenth century described hydrochloric acid under the name of " spirit of salt."   Glauber in 1648 obtained it from salt and sulfuric acid and gave it the name " muriatic acid " (from *muria, brine*). The free gas was first obtained and collected over mercury by Priestley in 1772, and Davy ascertained its composition in 1810.

Preparation.—Hydrochloric acid may be prepared:

1. By the direct union of its constituents, as when a mixture of equal volumes of hydrogen and chlorin is exposed to sunlight, a flame, an electric spark, or magnesium light : $H + Cl = HCl$ . . . . (1)

2. By the action of chlorin upon hydrogen compounds, such as water, hydrogen sulfid, ethylene, and oil of turpentine :

$$H_2O + Cl_2 = 2HCl + O \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

3. By the action of sulfuric acid upon chlorids :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl \quad . \quad . \quad . \quad . \quad (3)$$
$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl \quad . \quad . \quad . \quad . \quad (4)$$
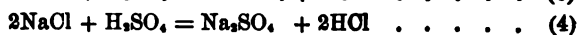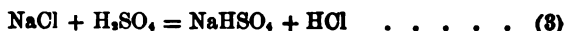
4. By the action of hydrogen upon certain metallic chlorids, such as silver chlorid :

$$AgCl + H = HCl + Ag \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The gas is best prepared by gently warming a mixture of six parts of common salt and eleven parts of sulfuric acid in a flask provided with safety- and delivery-tubes and wash-bottle.   The reaction is according to equation 3.   If a larger proportional amount of salt is used, the reaction of equation 4 takes place, but a high temperature is required to complete it.   The gas may be collected by displacement in dried bottles, or over mercury, or may be conveyed into bottles containing water in which it dissolves with great vigor.
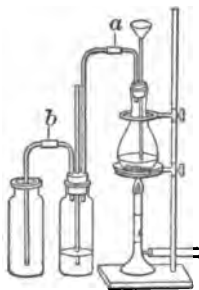
Fig. 57.

This reaction is a general one.   When an acid and a salt are brought together, they react, forming the other acid and the other salt, until the four compounds present are in equilibrium in accordance with the law of mass action.   If one of the compounds formed is volatile, and escapes, the equilibrium is disturbed and the action continues.   In this way even a strong acid may be generated

from its salts by the action of a weaker acid. In the case before us, the hydrogen chloride is conducted away and the action continues until the sodium chlorid is all decomposed, or until the reaction is complete.

Illustrations.—The direct union of hydrogen and chlorin may be shown by filling a jar with equal volumes of the two gases and bringing a lighted taper to its mouth. A violent explosion ensues and fumes of hydrochloric acid appear. (Equation 1.) The mixture is most easily obtained as follows: Fill two jars, the one with hydrogen and the other with chlorin, bring them mouth to mouth, the hydrogen above, and invert a few times. Both jars are now full of the mixture.

A pretty experiment may be made by filling small bulbs of thin glass with the mixed gases obtained by the electrolysis of hydrochloric acid and then sealing them. On being exposed to sunlight or magnesium light they explode with violence, shattering the glass. The bulbs must be kept in the dark, since the gases slowly unite in diffused daylight.

Lower into a jar of chlorin a jet of burning hydrogen and note the character of the flame and the fumes of HCl.

The commercial acid is chiefly obtained as a waste product of the soda manufacture. Salt and sulfuric acid being used, large quantities of hydrogen chlorid are evolved. The gas is conducted into towers filled with coke or bricks over which water continuously trickles. The gas is dissolved and the solution is drawn off below.

Physical Properties.—Hydrogen chlorid is a colorless gas with a pungent, suffocating odor and acid taste. It fumes strongly in the air, dissolving in the condensed moisture. Under a pressure of 40 atmospheres at 10° or 1 atmosphere at $-$ 80.3° it condenses to a colorless liquid of specific gravity 1.27 which boils at $-$ 80.3° and freezes at $-$ 113°. Its critical temperature is 52.3° and its critical pressure is 86 atmospheres. Being somewhat heavier than air, specific gravity 1.26, it is easily collected by displacement.

The gas is very soluble in water, one volume at 0° dissolving 503 volumes. As the temperature rises the solubility diminishes, the coefficient of solubility being 450 at 10°, 411 at 30°, and 364 at 50°. A solution saturated at 15° contains 42.9 per cent of the gas and has a specific gravity 1.212. If this solution be heated, the gas escapes until the temperature rises to 110°, when the liquid distils over. The distillate has a specific gravity of 1.104 and contains 20.24 per cent HCl, very nearly corresponding to the formula $HCl + 8H_2O$. This is not a definite compound, as the composition

of the distillate varies with the pressure. If the solution be cooled to − 40°, or if HCl be passed through the solution cooled to − 22°, crystals having the definite composition HCl + 2H$_2$O separate out. These melt and decompose at − 18°.

There is evidently chemical union between the hydrogen chlorid and the water, but just what the compound is has not been ascertained. The simplest hypothesis is that they combine molecule to molecule, chlorin taking the valence three and the formula having the structure ${H \atop H}>$Cl—O—H.

The aqueous solution, which is called *hydrochloric acid* and also *muriatic acid*, possesses all the properties of the gas and is even more active. It is a colorless liquid whose specific gravity depends upon the amount of gas in the solution. The strong acid of commerce has usually a specific gravity 1.16 and contains 32 per cent HCl, while the dilute acid has specific gravity 1.09 and contains 18.4 per cent HCl. The color of the commercial acid is due to impurities, chiefly chlorin, iron chlorid, and organic matters.

Illustrations.—Pour a few drops of strong sulfuric acid on a little common salt in a tube. Bring to the mouth of the tube a rod which has been dipped in ammonia: dense white fumes of ammonium chlorid arise.

Hydrogen chlorid may be liquefied as follows: Into the closed end of a strong tube bent three times zigzag at right angles place a few grams of ammonium chlorid, then introduce into the middle bend by means of a bent funnel-tube twice as much sulfuric acid. Draw out the tube with the blowpipe and close it so as to leave a thick wall. Let the tube cool, then incline it so as to bring together the acid and the chlorid. The HCl generated condenses to liquid under its own pressure. Under a gentle heat the liquid distils over into the empty limb of the tube, which should be immersed in a freezing mixture. The experiment should be made with care, as the tube is liable to burst under the great pressure within it.

The solubility of the gas may be shown by filling by displacement a bottle with the gas (dried by passing it through a tube containing calcium chlorid) and inverting it over water. The water rushes into the bottle as the gas dissolves. Test the solution with litmus paper.

Chemical Properties.—Hydrogen chlorid when dry does not seem to be very active, but in the presence of moisture it is one of the most energetic of chemical agents. It does not burn in the air and does not support combustion. It is very stable, but is decomposed by a strong electric current and by heat at 1500°.

The aqueous solution is intensely acid, reddens litmus, and has a burning sour taste. Its activity is mainly due to dissociation and

the presence of the hydrogen and chlorin ions. The hydrogen may
be replaced by nearly all the positive elements and radicals. It acts
not only with the metals but with the bases, the basic oxids, and
ammonia to form the binary salts called *chlorids*. It does not
readily act upon the non-metals. The following equations show
some of its characteristic reactions:

1. With metals : $HCl + Na = NaCl + H.$

2. With bases : $HCl + KHO = KCl + H_2O.$

3. With basic oxids : $2HCl + ZnO = ZnCl_2 + H_2O.$

4. With ammonia : $HCl + NH_3 = NH_4Cl.$

Nearly all the chlorids are soluble in water or weak acids. The
notable exceptions are the chlorids of silver, lead, and mercury.

Hydrogen and chlorin are both monads and hence they unite
atom to atom and volume to volume. The heat of the union is
22,000 calories. The thermal and volume equation is

$$H \quad + \quad Cl \quad = \quad HCl + 22,000 \text{ cal.}$$
$$1 \text{ vol.} + 1 \text{ vol.} = 2 \text{ vols.}$$
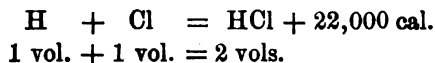
Hydrogen chlorid in water solution forms the ions $H\cdot$ and Cl'.
The dissociation is greater than that of any other compound except
nitric acid and the alkali hydroxids, to which it is about equal.
It is therefore the strongest of all acids except nitric acid. The
percentage of dissociation of the normal acid is 81, of the deci-
normal 94, of the centinormal 99, and of the millinormal 100.

Illustrations.—The inactivity of dry HCl may be shown by suspending
dry litmus paper in the dry gas. The color is not changed.

Its action with ammonia is seen when a few drops of ammonia are
added to a jar containing a few drops of hydrochloric acid.

To show its action with metals drop into a small quantity of the acid in
a tube fragments of sodium, zinc, iron, copper, etc.

To show its neutralizing action with bases place in a dish with a piece
of litmus paper a cubic centimeter of potassium hydroxid solution and add
the acid carefully until the blue color just changes to a faint red. The
solution is then neutral, that is contains only a salt and water, neither acid
nor base. Red spots made on the clothes by the acid may be removed with
ammonia.

The composition of HCl may be demonstrated by the following two ex-
periments : Pass the gas slowly over a piece of sodium heated in a glass
tube. (1) The sodium unites to the chlorin retaining it, and the hydrogen
passes on and may be collected and tested. (2) Let the gas be passed over
manganese dioxid heated in a tube. The hydrogen is retained and the
chlorin passes on :

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl.$$

The volume composition can be proven by electrolysis. Fill a decomposing apparatus with the strongest hydrochloric acid and pass a current from four Bunsen cells. The chlorin collects in the tube containing the positive electrode and the hydrogen in the other. Let the gases escape until the liquid is saturated with chlorin, then close the cocks and it will be seen that equal volumes collect in the two tubes.

Physiological Properties.—Hydrogen chlorid is a stifling acid gas which has a corrosive and irritating action upon the respiratory organs. The strong acid burns the skin and disorganizes tissues, but if largely diluted it may be taken into the stomach without injury.

Uses.—Hydrochloric acid has numerous uses in the arts and the laboratory. It is used in the manufacture of chlorin, chlorids, hydrogen, and bleaching-powder. Being a by-product of the soda manufacture, it is cheap and the quantity consumed is larger than that of any other acid except sulfuric acid.

Tests.—Hydrogen chlorid may be recognized by its odor, its acid action, its forming chlorids, and the dense fumes it makes with ammonia. The characteristic reagent for all soluble chlorids is silver nitrate, with which they form insoluble silver chlorid.

Chlorid Ion.—The chlorid ion Cl′ is univalent, colorless, and electronegative. It is quite active with other ions, but not with molecular compounds. It is physiologically wholesome and not poisonous. Its heat of formation from molecular chlorin is 40,300 calories. The common properties of the soluble chlorids are due to this ion.

HYDROGEN BROMID—HYDROBROMIC ACID.

Formula HBr. Molecular weight 81. Density 40.5. Specific gravity 2.81. Liter weighs 3.63 grams.

Preparation.—Hydrogen bromid does not occur free in nature. It is not so stable as hydrogen chlorid and therefore not so easily obtained. It may be prepared in the following ways:

1. By direct synthesis, H and Br uniting atom to atom and volume to volume with the development of 8440 units of heat :

$$H + Br = HBr + 8440 \text{ cal.} \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$1 \text{ vol.} + 1 \text{ vol.} = 2 \text{ vols.}$$
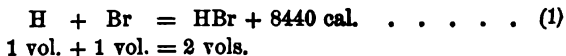
This action takes place only at a high temperature, or in the presence of platinum sponge, or under the influence of the electric spark.

2. By the action of bromin upon hydrogen sulfid when this gas is passed through bromin water: $Br_2 + H_2S = 2HBr + S$ . . . . (2)

3. By the action of phosphorus tribromid upon water :

$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr \quad . . . . . . (3)$$
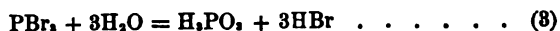
4. By the action of bromin upon water in the presence of phosphorus :

$$P + 5Br + 4H_2O = 5HBr + H_3PO_4 \quad . . . . . (4)$$
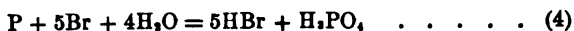
In this action the bromids of phosphorus are probably first formed and then decomposed by the water as follows :

$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr$$
$$PBr_5 + 4H_2O = H_3PO_4 + 5HBr$$
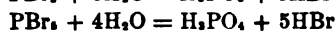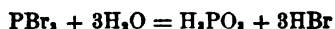
5. By the action of phosphoric acid upon bromids:

$$3KBr + H_3PO_4 = K_3PO_4 + 3HBr \quad . . . . . (5)$$
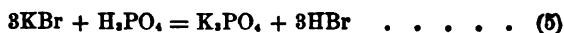
6. By the action of sulfuric acid upon bromids :

$$H_2SO_4 + 2KBr = K_2SO_4 + 2HBr . . . . . . (6)$$
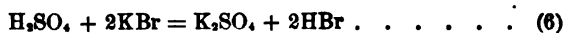
This action is not simple as in the case of the chlorids, but bromin is also set free, the hydrogen bromid being decomposed by oxygen coming from the sulfuric acid: $H_2SO_4 + 2HBr = SO_2 + 2H_2O + Br_2$. This decomposition may be prevented by having present some more powerful reducing agent, such as phosphorus or hydrogen sulfid.

7. By the action of bromin upon turpentine, melted paraffin, and other hydrocarbons. With turpentine the action is

$$C_{10}H_{16} + Br_2 = C_{10}H_8Br + HBr \quad . . . . . . (7)$$
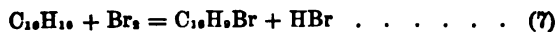
In the laboratory hydrogen bromid is conveniently prepared as follows: Place in a flask furnished with a separatory funnel-tube and a delivery-tube one part of amorphous phosphorus and two parts of water. Introduce bromin drop by drop from the funnel-tube and gently warm the flask. The gas may be passed through a U tube containing amorphous phosphorus to retain the bromin vapor which goes over. It is collected over mercury, or in dry jars, or conducted into water to make the solution.

A very simple method of showing the formation of HBr by direct synthesis is to pass hydrogen gas through bromin and ignite the escaping vapors. Dense fumes of hydrogen bromid are formed.

Physical Properties.—Hydrogen bromid is a colorless, fuming gas with a pungent, irritating odor and acid taste. Under pressure it condenses to a colorless liquid which boils at $-73.3°$ and freezes at $-87°$.

It is freely soluble in water, forming hydrobromic acid. The solution saturated at $0°$ contains 82 per cent of HBr and has a

specific gravity 1.78.   At 15° it contains 49.8 per cent of HBr and has a specific gravity 1.515.   Upon being heated it loses the gas
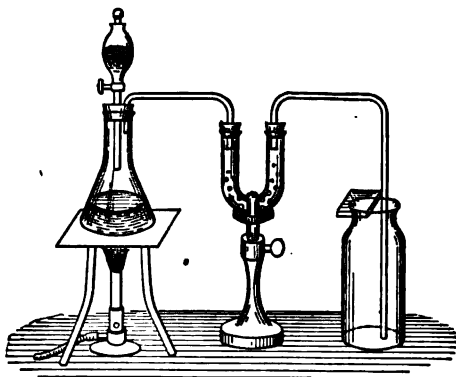
Fig. 58.

until a temperature of 125° is reached, when a liquid distils over having a specific gravity 1.47 and containing 47.8 per cent of HBr.

If the gas be passed through the solution cooled to − 20°, crystals separate which have the formula $HBr, 2H_2O$ and melt at 11°.

Chemical Properties.—Chemically, hydrogen bromid very closely resembles hydrogen chlorid.   It is less stable, decomposing at 800°, and the bromin is easily replaced by chlorin.   In the aqueous solution bromin is gradually set free by the dissolved oxygen: $2HBr + O = 2Br + H_2O$.   It acts upon metals and metallic oxids and hydroxids to form *bromids*.   The bromids are all soluble, except those of silver, lead, and mercury.

Tests and Uses.—Hydrogen bromid is recognized by its general properties and by its forming silver bromid with silver nitrate.   It is of little commercial importance, being used to a limited extent in laboratories and in medicine.

Bromid Ion.—Hydrobromic acid is almost as highly dissociated as hydrochloric acid, and hence but little inferior to it in strength.   The bromid ion Br′ is univalent, colorless, medicinal, non-poisonous, and strongly negative.   It gives the common properties to the bromids and closely resembles the chlorid ion by which it is replaced, thus:

$$Na \cdot, Br' + Cl = Na \cdot, Cl' + Br.$$
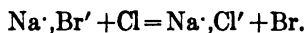
HYDROGEN IODID. HYDRIODIC ACID.

Formula HI. Molecular weight 128. Density 64. Specific gravity 4.4. Liter weighs 5.7 grams.

Preparation.—Hydrogen iodid is obtained by reactions exactly similar to those used in the preparation of hydrogen bromid. It is formed in the following ways:

1. By passing hydrogen and iodin vapor together through a red-hot tube containing platinum sponge. The reaction is endothermic :

$$H + I = HI - 6200 \text{ cal.} \quad \ldots \ldots \ldots (1)$$

2. By the action of phosphoric acid upon iodids :

$$H_3PO_4 + 3KI = K_3PO_4 + 3HI \quad \ldots \ldots (2)$$
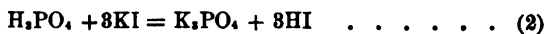
As with bromids, sulfuric acid cannot be used since I is set free.

3. By the action of phosphorus tri-iodid upon water:

$$PI_3 + 3H_2O = H_3PO_3 + 3HI \quad \ldots \ldots \ldots (3)$$

4. By passing hydrogen sulfid through water containing suspended iodin :

$$H_2S + I_2 = 2HI + S \quad \ldots \ldots \ldots (4)$$

5. By the action of iodin upon water in the presence of phosphorus :

$$P + 5I + 4H_2O = H_3PO_4 + 5HI \quad \ldots \ldots (5)$$

Hydrogen iodid is most conveniently prepared by the last reaction. Place in a flask one part of phosphorus and 15 parts of water and add by littles 20 parts of iodin, cooling the flask if necessary. The flask is then warmed and the gas collected as in the case of hydrogen bromid.

Physical Properties.—Hydrogen iodid is a colorless, fuming gas with a pungent odor, and is nearly four and a half times as heavy as air. It liquefies under a pressure of four atmospheres at 0°, melts at − 34°, and freezes at − 55°. It is quite soluble in water, forming the solution called *hydriodic acid*. The solution saturated at 0° is nearly twice as heavy as water, having a specific gravity 1.99 and containing 90 per cent HI. On being heated, the acid weakens until at 127° the distillate has a specific gravity 1.67 and contains 57.7 per cent of HI.

Chemical Properties.—Hydrogen iodid is quite unstable, beginning to decompose even at 180°. The iodin is replaced by all the other halogens: HI + Cl = HCl + I. The solution gradually oxidizes and is colored brown by the liberated iodin : $2HI + O = H_2O + I_2$. It cannot be collected over mercury be-

cause of the action, $2HI + 2Hg = Hg_2I_2 + H_2$. It forms *iodids* with many metals, oxids, and hydroxids. It is a powerful reducing agent, and as such finds many uses in laboratories.

While iodin is replaced by fluorin, chlorin, and bromin, the reverse action may take place in accordance with the law of mass action because of the lower volatility of the iodin compounds, as when sodium chlorid is evaporated with hydrogen iodid, $Na^·,Cl' + HI = Na^·,I' + HCl$.

Hydriodic acid is ionized to nearly the same extent as hydrochloric acid and has therefore about the same strength.

Iodid Ion.—The iodid ion I' is univalent, colorless, and negative. It gives the general characteristics to the soluble iodids. Iodin is quite soluble in solutions of iodids, coloring them brown. This is explained on the hypothesis that the molecular iodin combines with the iodid ion to form the brown complex ion I_3'.

COMPOUNDS OF THE HALOGENS WITH ONE ANOTHER.

Since the halogens are all strongly negative and chemically very much alike, they do not readily combine with one another. The few compounds that are formed are all unstable and chemically very active.

Bromin Chlorid, BrCl, is a volatile, orange-colored liquid obtained by direct union of the two elements. It dissolves in water and on cooling forms a crystalline hydrate which melts at 7°.

Iodin Pentafluorid, IF_5, is a colorless fuming liquid formed by the action of iodin upon silver fluorid.

Iodin Chlorid, ICl, is a reddish-brown liquid formed by the direct union of iodin with well-dried chlorin. It solidifies in the form of large red transparent prisms which melt ᵒt 25°. It boils at 101°, deliquesces in the air, and is decomposed by water.

Iodin Trichlorid, ICl_3, is a yellow crystalline solid formed by the action of an excess of dry chlorin upon iodin, or iodin chlorid, or hydriodic acid. It forms brilliant needle-shaped crystals which sublime readily and melt at 25°. When heated it dissociates into chlorin and iodin chlorid, but recombines on cooling.

Iodin Bromid, IBr, is a crystalline solid formed by the union of the elements. It melts at about 30°.

Iodin Tribromid, IBr_3, is a dark-colored liquid.

CHAPTER XXIII.

OXIDS AND ACIDS OF THE HALOGENS.

GENERAL CHARACTERISTICS.

Affinity and Stability.—While the halogens have a strong affinity for hydrogen, their attraction for oxygen and hydroxyl is small, and all the oxids and acids are unstable. The stability of the compounds containing oxygen increases with the atomic weight, the iodin compounds being most stable and most numerous, while fluorin forms neither oxid nor acid. In the higher oxygen compounds chlorin and bromin are displaced by iodin, while in the haloid acids the reverse action takes place. Furthermore, the stability increases as the amount of oxygen increases. The lower acids, $HClO$, $HBrO$, and $HClO_2$, and their salts are unstable, weakly acid, and are decomposed by CO_2, while the more highly oxygenated acids, $HClO_3$, $HBrO_3$, and HIO_3, are quite stable, but when decomposed develop great energy. The acids are more stable than the oxids, but are all more or less ionized.

Thermal Characters.—The instability and chemical behavior of these compounds are illustrated by their thermal characters. The oxids of chlorin and bromin are all endothermic, while iodin pentoxid is exothermic. Some of the thermal equations are as follows:

$$(Cl_2, O\text{---gas}) = -17,800 \text{ cal.} \quad (Cl_2, O_5\text{---solution}) = -20,400 \text{ cal.}$$
$$(Br_2, O_5\text{---solution}) = -43,500 \text{ cal.} \quad (I_2, O_5\text{---solid}) = +44,800 \text{ cal.}$$
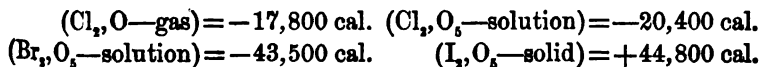
These equations explain the stability of the iodin compound and also why the anhydrous pentoxids of chlorin and bromin cannot be formed. The heat of formation of the principal acids in dilute aqueous solution and their potassium salts is as follows:

$$(H,Cl,O_3,Aq.) = 23,900 \text{ cal.} \quad (K,Cl,O_3) = 95,900 \text{ cal.}$$
$$(H,Br,O_3,Aq.) = 12,400 \text{ cal.} \quad (K,Br,O_3) = 87,600 \text{ cal.}$$
$$(H,I,O_3,Aq.) = 55,700 \text{ cal.} \quad (K,I,O_3) = 128,400 \text{ cal.}$$
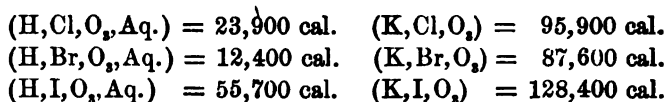
These equations show why chlorin and bromin are displaced from their acids by iodin and why bromin does not displace chlorin in chloric acid.

Valence and Structure.—The halogens when they act as negatives in binaries are monads. When combined with oxygen and hydroxyl they have valences varying from one to seven. Chlorin will then theoretically have four regular oxids as follows:

Name.	Molecular Formula.	Structural Formula.
Hypochlorous oxid	$Cl_2'O$	$Cl{-}O{-}Cl$
Chlorous oxid	$Cl_2'''O_3$	$O{=}Cl{-}O{-}Cl{=}O$
Chloric oxid	$Cl_2^VO_5$	$\underset{\displaystyle O}{\overset{\displaystyle O \atop \parallel}{O{=}Cl}}{-}O{-}\underset{}{\overset{\displaystyle O \atop \parallel}{Cl{=}O}}$
Perchloric oxid	$Cl_2^{VII}O_7$	$O{=}\overset{\displaystyle O \atop \parallel}{\underset{\displaystyle \parallel \atop O}{Cl}}{-}O{-}\overset{\displaystyle O \atop \parallel}{\underset{\displaystyle \parallel \atop O}{Cl}}{=}O$

All these oxids have been prepared or are represented in the corresponding acids and the salts derived from them. Exactly similar compounds of bromin and iodin may be supposed to exist, although but one, I_2O_5, has really been formed.

The acids of chlorin may be taken to illustrate the acids of the group.

Name.	Molecular Formula.	Structural Formula.
Hypochlorous acid	$HCl'O$	$H{-}O{-}Cl$
Chlorous acid	$HCl'''O_2$	$H{-}O{-}Cl{=}O$
Chloric acid	HCl^VO_3	$H{-}O{-}Cl{\big\langle}{\overset{\displaystyle O}{\underset{\displaystyle O}{}}}$
Perchloric acid	$HCl^{VII}O_4$	$H{-}O{-}\overset{\displaystyle O \atop \parallel}{\underset{\displaystyle \parallel \atop O}{Cl}}{=}O$

These acids are formed from the oxids by union with water, one molecule of the oxid and one of water making two of the acid:

$$Cl_2O_3 + H_2O = 2HClO_2$$

$$\underset{O=Cl}{\overset{O=Cl}{}}{>}O + O{<}\underset{H}{\overset{H}{}} = \underset{H{-}O{-}Cl{=}O}{\overset{H{-}O{-}Cl{=}O}{}}$$
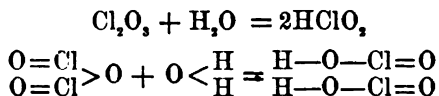
Ortho and Meta Acids.—The tendency of acids is, as we have seen, to contain the smallest possible amount of hydrogen. The above acids of chlorin are all monobasic. The first is ortho, the second monometa, the third dimeta, and the fourth trimeta. They dissolve in water in all proportions and no doubt form the hydrated acids, but these cannot generally be isolated as such. Of the theoretical perchloric acids given below the last three have been prepared. They are obtained by subtracting successive molecules of water from the hypothetical orthoperchloric acid in which all the seven points of the chlorin atom are united to hydroxyl:

Orthoperchloric acid $\quad H_7Cl^{vu}O_7 \qquad$

Monometaperchloric acid $\quad H_5Cl^{vu}O_6 \qquad$

Dimetaperchloric acid $\quad H_3Cl^{vu}O_5 \qquad$

Trimetaperchloric acid $\quad HCl^{vu}O_4 \qquad$
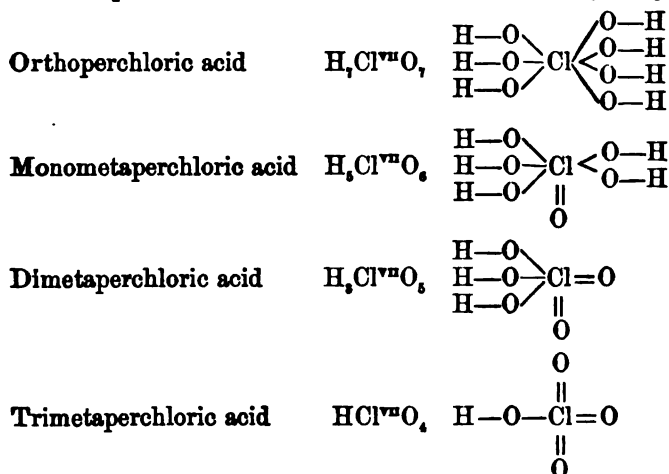
Salts.—The salts of the halogen acids are usually colorless crystalline solids which are quite unstable. They are strong oxidizers and make detonating mixtures with combustibles. Only two are of any commercial importance, potassium chlorate and calcium hypochlorite (chlorid of lime). The periodates are of considerable theoretical interest.

OXIDS AND ACIDS OF CHLORIN.

Oxygen and chlorin do not unite directly, but by indirect methods three oxids and three acids can be formed, all unstable and strong oxidizing and bleaching agents:

Hypochlorous oxid. . . . . . Cl_2O Hypochlorous acid. . . . . . HClO
Chlorin tetroxid. . . . . Cl_2O_4 Chloric acid. . . . . $HClO_3$
Perchloric oxid . . . . Cl_2O_7 Perchloric acid. . . . . $HClO_4$

HYPOCHLOROUS OXID (CHLORIN MONOXID).

Formula Cl_2O. Molecular weight 87. Density 43.5.

Preparation.—Hypochlorous oxid was discovered by Ballard in 1834. It is prepared by conducting dry chlorin over dry precipitated mercuric oxid kept well cooled. It is condensed to a liquid by passing through a bent tube immersed in a freezing mixture. Mercuric oxychlorid is formed in the reaction, which is as follows:

$$2HgO + 2Cl_2 = HgO,HgCl_2 + Cl_2O.$$
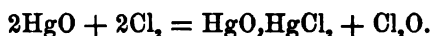
Physical Properties.—Hypochlorous oxid is a reddish-yellow gas with a penetrating odor resembling that of chlorin. It is poisonous and irritating to the respiratory organs. It is three times as heavy as the air, its density being 43.5 as required by the formula. When strongly cooled it condenses to an orange-colored liquid which boils at $-19°$. It dissolves freely in water, 100 volumes to one of water, to form hypochlorous acid.

Chemical Properties.—Hypochlorous oxid, gas or liquid, is unstable and highly explosive. It is decomposed by heat, flame, electric spark, and sunlight, and even by a slight jar, as in pouring from one vessel to another. Two volumes of the gas yield one volume of oxygen and two of chlorin: $Cl_2O = Cl_2 + O$.

It oxidizes and bleaches strongly. Sulfur, phosphorus, the alkali metals, and organic substances take fire in it, or cause it to explode. It oxidizes hydrochloric acid, forming water and setting chlorin free: $2HCl + Cl_2O = 2Cl_2 + H_2O$. With calcium chlorid and alkaline hydroxids it forms hypochlorites:

$$CaCl_2 + 2Cl_2O = CaCl_2O_2 + 2Cl_2. \quad 2KHO + Cl_2O = 2KClO + H_2O.$$
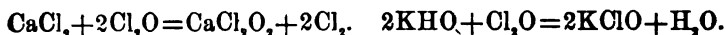
CHLORIN TETROXID (CHLORIN DIOXID, CHLORIN PEROXID).

Formula Cl_2O_4 or ClO_2. Molecular weight 134.8 or 67.4. Density 33.7.

Preparation.—Chlorin tetroxid was discovered by Davy in 1814. It is prepared by the action of sulfuric, hydrochloric, or oxalic acid upon potassium chlorate according to the following reactions:

1. $3KClO_3 + 2H_2SO_4 = KClO_4 + 2HKSO_4 + H_2O + 2ClO_2$
2. $4KClO_3 + 12HCl = 4KCl + 6H_2O + 9Cl + 3ClO_2$
3. $2KClO_3 + 2H_2C_2O_4 = K_2C_2O_4 + 2H_2O + 2CO_2 + 2ClO_2$

By the second reaction the gas is obtained mixed with three times its volume of chlorin. This mixture was formerly supposed

to be a compound and was called *euchlorin.* It is a powerful oxi-- dizing and bleaching agent and a vigorous disinfectant. The gas prepared by the third method is mixed with an equal volume of carbon dioxid.

The gas is collected by displacement of air, or is conducted into water to form the solution, or is condensed to a liquid by passing through a bent tube immersed in a freezing mixture.

Illustrations.—Add a gram of potassium chlorate to a few cubic centi- meters of sulfuric acid in a test-tube held by a support and gently warm. The gas collects in the tube, displacing the air. If the action becomes too rapid, cool the tube by bringing under it a beaker of water. When the tube is full, bring a flame to its mouth and the gas decomposes with a smart explosion.

Place crystals of potassium chlorate in a tube or flask, add hydrochloric acid and warm gently. The euchlorin is collected by displacement.

Physical Properties.—Chlorin tetroxid is a greenish-yellow gas a little more than twice as heavy as the air. Its odor is unpleasant and irritating and it is poisonous, producing headache when breathed even in very small quantities. When cooled it condenses to a red- dish-brown liquid which boils at 10°, and freezes at − 79° to an orange-colored crystalline solid. At 4° water dissolves about 20 volumes of the gas, forming a yellow solution, and at lower tem- peratures a crystalline hydrate separates.

Chemical Properties.—Chlorin tetroxid is very unstable, decom- posing with violence under the influence of heat, the electric spark, or contact with organic matter. It can be kept in the dark, but in the light slowly separates into oxygen and chlorin. It is a strong oxidizer, many combustibles, as hydrogen sulfid, phosphorus, ether, and sugar, taking fire in it spontaneously. Its solution is decolor- ized by alkali hydroxids with the formation of both the chlorite and chlorate of the alkali: $2KOH + 2ClO_2 = KClO_2 + KClO_3 + H_2O$.

The gas density of chlorin tetroxid at 12° is 33.7, which indi- cates the formula ClO_2, an unsaturated radical. The probability is, however, that this is the result of dissociation and that at lower temperatures the formula is Cl_2O_4. Two structures have been given to this formula. As a union of two radicals, ClO_2, it may be written $O=Cl—Cl=O$. Its behavior with the alkali hydroxids mentioned
$$\underset{O}{\overset{\|}{}} \quad \underset{O}{\overset{\|}{}}$$

above favors the theory that it is a chlorous chloric oxid, one atom of chlorin being trivalent while the other is pentavalent, and that the formula is O=Cl—O—Cl=O.

$$\overset{\|}{O}$$

Illustrations.—The oxidizing action of chlorin tetroxid may be shown by the following experiments :

Place a mixture of pulverized potassium chlorate and granulated sugar on a brick or board and add to it a drop of sulfuric acid. The tetroxid set free ignites the sugar, which burns with vigor in oxygen taken from the chlorate.

Add some crystals of potassium chlorate to a conical glass containing water and drop in a small piece of phosphorus, then convey to the crystals by means of a pipet a few drops of sulfuric acid. The phosphorus burns under the water in the tetroxid set free.

Lower a jet of hydrogen sulfid in a jar filled with euchlorin. The jet ignites spontaneously and continues to burn in the gas.

PERCHLORIC OXID (CHLORIN HEPTOXID).

Formula Cl_2O_7. Molecular weight 182.8.

Preparation.—Perchloric oxid is prepared by the action of phosphoric oxid upon perchloric acid. The acid is dropped upon the pentoxid in a retort kept cooled to — 10°. After standing twenty-four hours the mixture is distilled on a water-bath at 85°. The reaction is probably as follows:

$$2HClO_4 + P_2O_5 = 2HPO_3 + Cl_2O_7.$$
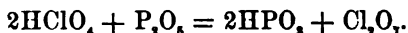
Properties.—Perchloric oxid is a colorless, very volatile, oily liquid which boils at 82°. It is more stable than the other oxids of chlorin, but explodes with great violence when heated or exposed to a shock. When well cooled it does not attack paper, sulfur, nor phosphorus. It is dangerous and must be handled with great care.

HYPOCHLOROUS ACID.

Formula $HClO$. Molecular weight 52.4.

Preparation.—Hypochlorous acid is always obtained in aqueous solution from which the pure acid cannot be separated. It may be prepared in the following ways:

1. By the solution of hypochlorous oxid in water:

$$Cl_2O + H_2O = 2HClO.$$

2. By conducting chlorin into solution of alkali hydroxide:

$$KOH + Cl_2 = KCl + HClO.$$

8. By allowing chlorin to bubble through water containing mercuric oxid or calcium carbonate in suspension :

$$HgO + H_2O + 2Cl_2 = HgCl_2 + 2HClO.$$
$$CaCO_3 + H_2O + 2Cl_2 = CaCl_2 + CO_2 + 2HClO.$$
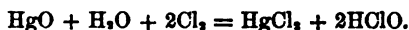
4. By passing carbon dioxid through a mixture of water and bleaching-powder :

$$2Ca(OCl)Cl + CO_2 + H_2O = CaCl_2 + CaCO_3 + 2HClO.$$
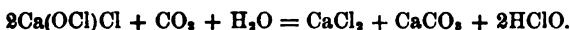
Properties.—The strongest solutions of hypochlorous acid have a yellow color and a strong chlorous smell. They are quite unstable, decomposing slowly in the dark and more rapidly in the light. Dilute solutions keep better and may be distilled.

Because of the readiness with which hypochlorous acid breaks up into hydrogen chlorid and nascent oxygen, $HClO = HCl + O$, it is a powerful bleaching and oxidizing agent and disinfectant. It decomposes hydrogen chlorid, silver oxid, and hydrogen sulfid, giving chlorin in the first case, oxygen in the second, and sulfur in the third:

$$HClO + HCl = H_2O + Cl_2.$$
$$Ag_2O + 2HClO = 2AgCl + H_2O + O_2.$$
$$H_2S + HClO = H_2O + HCl + S.$$
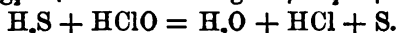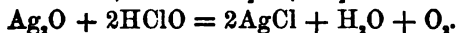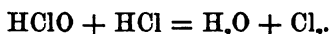
Uses and Tests.—Hypochlorous acid is used for bleaching cotton and linen goods. It cannot be used with silks and woolens because it colors them yellow. It is distinguished from chlorin as follows: When shaken with mercury it precipitates $HgO,HgCl_2$, and hypochlorites precipitate.HgO, both of which are soluble in hydrochloric acid; chlorin forms insoluble $HgCl_2$.

Hypochlorites.—Hypochlorites are formed by the action of chlorin in the cold upon strong bases, such as potassium hydroxid and lime, by reactions as follows:

$$2KHO + Cl_2 = KCl + H_2O + KClO \quad . \quad . \quad . \quad (1)$$
$$2Ca(HO)_2 + 4Cl = CaCl_2 + 2H_2O + Ca(ClO)_2 . \quad . \quad (2)$$
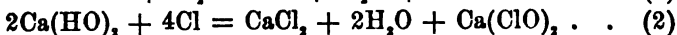
When hypochlorites are treated with acids, hypochlorous acid is formed:

$$KClO + HCl = KCl + HClO,$$
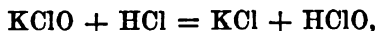
and this in turn is decomposed by the acid setting free chlorin:

$$HClO + HCl = H_2O + Cl_2.$$
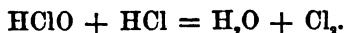
Thus the hypochlorites like the acid are bleaching and oxidizing agents.   Being more stable and more easily handled, they are used in preference to the acid.   There are two principal commercial forms: *Eau de Javelles,* which is a solution of the chlorid and hypochlorite of potassium formed according to equation 1, and the mixture of calcium chlorid and calcium hypochlorite, commonly called *chlorid of lime* or *bleaching-powder*, prepared according to equation 2.

Eau de Javelles was first prepared by Berthollet about 1785.   He established a factory at Javelles and hence the name.   In 1798 Tennant found that lime answered the same purpose as potash, and as it was much cheaper chlorid of lime soon became the chief commercial bleaching article.

Chlorites.—Neither *Chlorous Oxid,* $Cl_2'''O_3$, nor *Chlorous Acid*, $HCl'''O_2$, has been prepared.   Chlorin trioxid has usually been described as being formed when nitric acid acts upon potassium chlorate in the presence of a reducing agent such as arsenic trioxid, sugar, or tartaric acid.   Recent researches have shown that the gas thus produced is a mixture of chlorin and chlorin tetroxid.

Numerous chlorites are known.   They are all unstable and oxidize and bleach vigorously.   The chlorites of the alkalies dissolve easily, while those of the heavy metals are difficultly soluble. The chlorites of silver and lead are precipitated from solutions of alkali chlorites by silver nitrate and lead acetate:

$$AgNO_3 + KClO_2 = KNO_3 + AgClO_2.$$
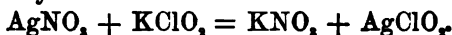
<div align="center">CHLORIC ACID.</div>

<div align="center">Formula $HClO_3$.   Molecular weight 84.4.</div>

History and Preparation.—This, the most important of the acids of chlorin, was discovered by Berthollet in 1786.   It has never been obtained in the pure state, but aqueous solutions are prepared as follows:

1. By the action of light upon moist oxids of chlorin.
2. By the action of acids upon chlorates :

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$
$$H_2SiF_6 + 2KClO_3 = K_2SiF_6 + 2HClO_3.$$
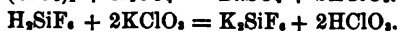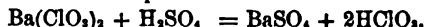
It is best prepared by mixing a solution of barium chlorate with exactly the equivalent amount of dilute sulfuric acid.   The barium sulfate is filtered off and the solution concentrated over sulfuric acid in vacuo.

Physical Properties.—The concentrated chloric acid is a colorless, syrupy liquid which has a specific gravity 1.28 and contains 40 per cent of the acid. It has a pungent, chlorous smell and a harsh acid taste.

Chemical Properties.—Chloric acid is so unstable that on further concentration of the strong solution, or on being heated, it decomposes, evolving chlorin and oxygen and forming perchloric acid and water:

$$3HClO_3 = Cl_2 + O_4 + HClO_4 + H_2O.$$
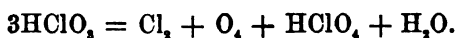
It bleaches strongly and is such an active oxidizer that it sets fire to phosphorus, sulfur, alcohol, paper, and organic matters generally. It is decomposed by hydrochloric acid into chlorin and water:

$$HClO_3 + 5HCl = 3H_2O + 6Cl.$$
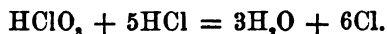
Chloric acid is monobasic and dimeta. The ortho acid, H_5ClO_5, and the monometa acid, H_3ClO_4, have not been separated nor are their salts known.

Chlorates.—Chlorates are formed by the action of chlorin in excess upon alkali hydroxids with the aid of heat:

$$6Cl + 6KHO = 5KCl + 3H_2O + KClO_3.$$

Or by the electrolysis of solutions of chlorids:

$$KCl + 3H_2O = KClO_3 + 3H_2.$$
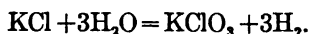
The chlorates are usually white crystalline salts soluble in water and many of them are deliquescent. They are more stable than the acid, but are strong oxidizers and with combustibles make mixtures which are exploded by concussion or heat. They yield perchlorates when decomposed by heat.

Illustrations.—To show the instability and oxidizing action of chlorates mix a very little finely powdered potassium chlorate with an equal quantity of sugar or sulfur, wrap tightly in paper and strike with a hammer.

PERCHLORIC ACID.

Formula $HClO_4$. Molecular weight 100.4.

History and Preparation.—Perchloric acid was discovered by Stadion in 1815. It is formed, as we have already seen, by the decomposition of chloric acid by heat. It is best prepared by distilling a mixture of one part of potassium perchlorate with four parts of sulfuric acid:

$$2KClO_4 + H_2SO_4 = K_2SO_4 + 2HClO_4.$$
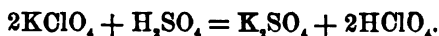
The distillation begins at 110°, and the first liquid that comes over is pure dimeta perchloric acid.

Physical Properties.—Perchloric acid is a colorless or slightly yellow fuming mobile liquid of specific gravity 1.78 at 15°. It boils at 110°, and when strongly cooled becomes a solid which melts at 15°. When dropped in water it gives a hissing sound and heat is evolved. It dissolves in water in all proportions.

Chemical Properties.—Perchloric acid when freshly prepared is more stable than the other acids of chlorin. After standing some days even in the dark, it is very unstable and highly explosive. When distilled it decomposes, darkens in color, and finally explodes. It bleaches and oxidizes strongly and decomposes with violence in contact with combustibles. It burns the skin, producing painful sores.

Perchloric acid is monobasic and trimeta. With one molecule of water it forms the dimeta acid H_3ClO_5, a colorless solid which melts at 50° and forms long needle-shaped crystals. When this is heated it separates into the trimeta and monometa perchloric acids $2H_3ClO_5 = HClO_4 + H_3ClO_6$, the first of which distils over, and this reaction may be conveniently used for the preparation of pure perchloric acid. The dihydrated or monometa perchloric acid is an oily liquid which boils at 208°. The trihydrated or ortho acid, $HClO_4 3H_2O = H_7ClO_7$, has not been isolated.

Illustrations.—To show the preparation and properties of perchloric acid, distil in a small retort a mixture of dry potassium perchlorate and recently boiled sulfuric acid. As the first drops of liquid fall from the neck of the retort note the fumes; let them fall in water and note the hissing sound; receive them on paper or freshly ignited charcoal and note the explosion. Collect the distillate in a receiver until the crystalline hydrate forms. Use small quantities and conduct the operation with care.

Perchlorates. —All the perchlorates are salts of the monobasic acid. They are soluble in water and a few of them are deliquescent. The most important one is potassium perchlorate, which is at the same time, with the exception of the rubidium salt, the least soluble, one part requiring 58 parts of water. The perchlorates are unstable, oxidize vigorously, and with combustibles make detonating mixtures.

The perchlorates are distinguished from the chlorates as follows:

1. They decompose at higher temperatures than the chlorates.
2. They are not acted upon by hydrochloric acid.
3. They do not yield Cl_2O_4 with sulfuric acid.

OXIDS AND ACIDS OF BROMIN.

No oxids of bromin have been prepared. Two of the acids are certainly known, and a third, perbromic, is said to have been formed. They are as follows:

| Hypobromous acid | $HBr'O$ | Bromic acid | HBr^vO_3 |
| Perbromic acid | $HBr^{vii}O_4$ | | |

Bromous acid and its salts are unknown.

HYPOBROMOUS ACID.

Formula HBrO. Molecular weight 97.

Preparation.—Hypobromous acid is formed by the action of bromin upon mercuric oxid in the presence of water:

$$HgO + 2Br_2 + H_2O = HgBr_2 + 2HBrO.$$
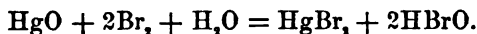
The precipitated mercuric oxid is shaken with bromin water and the mixture distilled *in vacuo* at a temperature below 30°.

Properties.—Hypobromous acid is a pale yellow unstable liquid. It bleaches and oxidizes and has other properties altogether similar to those of hypochlorous acid. The *hypobromites* are similar to the hypochlorites. When bromin acts upon lime there is produced a mixture of calcium bromid, $CaBr_2$, and calcium hypobromite, $Ca(BrO)_2$, called *bromid of lime*, which is similar in properties to the corresponding chlorid of lime.

BROMIC ACID.

Formula $HBrO_3$. Molecular weight 129.

Preparation.—Aqueous solutions of bromic acid are prepared as follows:

1. By the action of bromin upon silver bromate in the presence of water:

$$5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3.$$

The silver bromid settles and the acid solution is poured off.

2. By the action of sulfuric acid upon barium bromate in molecular proportions : $H_2SO_4 + Ba(BrO_3)_2 = BaSO_4 + 2HBrO_3$. The solution is separated from the precipitate by decantation.

3. By the action of chlorin upon bromin water :

$$5Cl_2 + Br_2 + 6H_2O = 10HCl + 2HBrO_3.$$
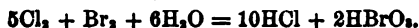
This gives a mixture of hydrochloric and bromic acids.

Properties.—Bromic acid in solution decomposes at 100°, evolving bromin and oxygen, but in vacuo it may be concentrated until the solution contains 50.6 per cent of $HBrO_3$. It is unstable, bleaches and oxidizes, and is decomposed by combustibles and reducing agents.

Bromates.—Bromates are formed by the action of bromin upon alkali hydroxids: $6KHO + 3Br_2 = 5KBr + 3H_2O + KBrO_3$. They are mostly crystalline solids difficultly soluble in water. They are decomposed by heat, yielding a bromid and oxygen, but no perbromate.

PERBROMIC ACID.

Formula $HBrO_4$.   Molecular weight 145.

Preparation.—Perbromic acid is said to be formed when bromin vapor acts upon perchloric acid, the bromin replacing the chlorin :

$$Br + HClO_4 = Cl + HBrO_4.$$
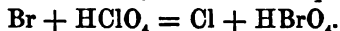
The reaction has not been well investigated and there is some doubt as to the existence of either the acid or its salts.

OXIDS AND ACIDS OF IODIN.

One oxid and two acids of iodin are known :

Iodic oxid $I_2^VO_5$.   Iodic acid HI^VO_3.   Periodic acid $HI^{VII}O_4$.

IODIC OXID (IODIN PENTOXID).

Formula I_2O_5.   Molecular weight 302.

Preparation.—Iodic oxid is prepared by heating iodic acid to 170° :

$$2HIO_3 = H_2O + I_2O_5.$$

Properties.—Iodic oxid is a white crystalline solid which melts at 300° and decomposes into iodin and oxygen. It has a specific gravity 4.487 and dissolves in water with vigor, forming iodic acid. It is the only halogen oxid whose formation is exothermic, and it is more stable than any of the others.

IODIC ACID.

Formula HIO_3. Molecular weight 176.

Preparation.—Iodic acid may be prepared in the following ways:

1. By adding water to iodic oxid: $H_2O + I_2O_5 = 2HIO_3$.

2. By the action of sulfuric acid upon barium iodate in molecular proportions: $H_2SO_4 + Ba(IO_3)_2 = BaSO_4 + 2HIO_3$. The acid solution is decanted from the precipitated barium sulfate and concentrated at 100°.

3. By the action of chlorin upon iodin in the presence of water:

$$5Cl + I + 3H_2O = 5HCl + HIO_3.$$
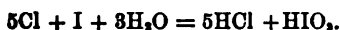
The HCl is removed with precipitated silver oxid and the silver chlorid separated by filtration.

4. By the action of iodin upon chloric or bromic acid, showing the ability of iodin to displace chlorin and bromin: $I + HClO_3 = Cl + HIO_3$.

5. Most conveniently by heating iodin with fuming nitric acid and continuing the heat until the water and oxids of nitrogen are expelled:

$$I + 3HNO_3 = H_2O + N_2O_3 + NO_2 + HIO_3.$$
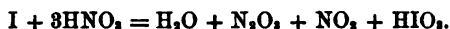
Properties.—Iodic acid is a white crystalline solid of specific gravity 4.629 at 0°. It is insoluble in alcohol, but dissolves in water in all proportions. No definite hydrated acids have been separated. The concentrated solution boils at 104°, and is a less vigorous bleaching and oxidizing agent than the acids of chlorin and bromin. It does not color starch blue except in the presence of a reducing agent, such as sulfurous oxid, hydrogen sulfid, or hydrogen iodid. It is decomposed by HI through the reducing action of the hydrogen ion $H·,IO_3' + 5H·,I' = 3H_2O + 3I_2$.

Illustration.—To a dilute solution of iodic acid add a little starch paste, then some sulfurous acid. In a few moments the blue color appears.

Iodates.—Iodates are formed by the action of a base upon iodic acid, or by the action of iodin upon alkali hydroxids:

$$3I_2 + 6KHO = 3H_2O + 5KI + KIO_3.$$

They are generally insoluble in water except the alkali iodates. On being heated they decompose, yielding oxygen and an iodid, or oxygen and iodin and a metal or metallic oxid, thus:

$$KIO_3 = KI + O_3. \quad Ba(IO_3)_2 = BaO + I_2 + O_5.$$
$$AgIO_3 = Ag + I + O_3.$$
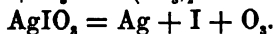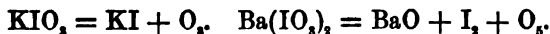
While iodic acid is monobasic and can only give normal salts, the alkali iodates form molecular compounds with iodic acid, giving the so-called *acid iodates*, thus: normal potassium iodate,

KIO_3; acid potassium iodate, KIO_3,HIO_3; di-acid potassium iodate, $KIO_3,2HIO_3$.

PERIODIC ACID.

Formula $HI^{vn}O_4$ or $H_5I^{vn}O_6$. Molecular weight 192 or 228.

Preparation.—Periodic acid is formed by the action of iodin upon perchloric acid: $2HClO_4 + I_2 = 2HIO_4 + Cl_2$. On evaporating the solution the dihydrated or monometa acid, $HIO_4,2H_2O = H_5IO_6$, crystallizes out. This is the only free periodic acid known. The normal or trimeta acid, HIO_4, cannot be obtained from it, as it decomposes on further evaporation. The acid with one of its silver salts is formed by boiling silver periodate with water:

$$4AgIO_4 + 5H_2O = Ag_4I_2O_9 + 2H_5IO_6.$$
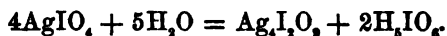
Properties.—The monometa or dihydrated periodic acid is colorless, crystalline, and deliquescent. It melts at 133° and decomposes at 150° into iodic oxid, water, and oxygen: $2H_5IO_6 = I_2O_5 + 5H_2O + O_3$. Its solution is acid and is like iodic acid in bleaching and oxidizing actions.

Periodates.—Periodic acid forms numerous salts which are best understood by supposing them to be derived from hypothetical acids as follows:

Orthoperiodic acid, H_7IO_7;   Monometaperiodic acid, H_5IO_6;
Dimetaperiodic acid, H_3IO_5;   Trimetaperiodic acid, HIO_4.

Each of these is obtained from the preceding one by subtracting, or from the following one by adding, a molecule of water. Others called diperiodic acids are obtained by taking a molecule of water from two molecules of the acid:

$$2H_5IO_6 - H_2O = H_8I_2O_{11}. \quad 2H_3IO_5 - H_2O = H_4I_2O_9.$$
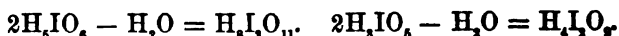
Examples of salts of these acids are:

Monometa, pentabasic, $Na_2H_3IO_6$;   Dimeta, tribasic, Ag_3IO_5;
Trimeta, monobasic, $NaIO_4$;   Diperiodic, octobasic, $Zn_4I_2O_{11}$.

The periodates are generally difficultly soluble and are like the acids in properties. They are variously obtained; as by heating the iodates, or by the oxidizing action of chlorin in the presence of an alkali:

$$5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 8I + 18O.$$
$$NaIO_3 + 3NaHO + Cl_2 = Na_2H_3IO_6 + 2NaCl.$$
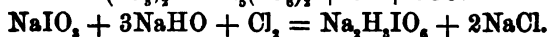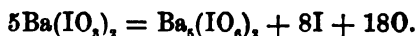
The Oxyions of the Halogens.—The acid ions formed by the union of the halogens with oxygen are all colorless, unstable, and quite active. The dissociation of the acids is various, being high in those in which the valence of the halogen is high and low in the others. The more common ions are as follows:

Hypochlorite, ClO'; chlorite, ClO_2'; chlorate, ClO_3'; perchlorate, ClO_4'.

Hypobromite, BrO'; bromate, BrO_3'.

Iodate, IO_3'; periodate, IO_4'.

The halogens also form complex ions with certain metals and metalloids, two atoms acting like oxygen with a valence two. These ions are found in the haloacids and the halosalts.

CHAPTER XXIV. ✦

GROUP VI B. THE SULFOIDS. SULFUR GROUP.

Oxygen 16. Sulfur 32. Selenium 79. Tellurium 127.

GENERAL PROPERTIES.

WHILE in this group the elements are closely related, oxygen has some exceptional properties. It is a gas, while the others are solids; its valence is always two, while the others exhibit the valences two, four, and six; it is negative to all elements, while the rest of the group are less negative than the halogens. Sulfur is strongly negative, but selenium and tellurium are near the borderland between positive and negative elements, tellurium even acting as a positive to form salts such as $Te^{IV}(SO_4)_2$.

The gradation of properties is well marked. As the atomic weight increases, the specific gravity, melting-point, and boiling-point increase, while the chemical activity, abundance of the element, and number of compounds diminish. Some of the leading properties are given in the following table:

	Oxygen.	Sulfur.	Selenium.	Tellurium.
Atomic weight	16	32	79	127
Specific gravity........	gas	2.0	4.5	6.26
Melting-point	....	114.5°	217°	452°
Boiling-point........	− 181°	448°	680°	white heat
Heat of union with H_2	58,780 cal.	2700 cal.	− 11,100 cal.	....
Allotropes............	2	4	4	....

The compounds of these elements are exactly analogous. Those of oxygen are most numerous and those of tellurium least so. They unite readily with hydrogen and with one another except selenium with tellurium. They have a strong affinity for the metals forming oxids, sulfids, selenids, and tellurids. They

262

have but little attraction for the halogens and form unstable compounds with them because so near to them in electric quality. The normal valence is II, the acidic valence VI.

A few typical compounds are here given:

	Oxygen.	Sulfur.	Selenium.	Tellurium.
With H.........	H_2O	H_2S	H_2Se	H_2Te
With O..........	....	SO_2 SO_3	SeO_2 SeO_3	TeO_2 TeO_3
With Cl.........	Cl_2O —	SCl_2 SCl_4	$SeCl_2$ $SeCl_4$	$TeCl_2$ $TeCl_4$
With Na.	Na_2O	Na_2S	Na_2Se	—
With Fe........	FeO	FeS	$FeSe$	$FeTe$
Acids...........	....	H_2SO_4	H_2SeO_4	H_2TeO_4

Oxygen and its compounds with hydrogen and the halogens have already been treated. The remainder of this chapter will be given to the discussion of sulfur, selenium, and tellurium, and their compounds with all the elements heretofore studied.

SULFUR.

Symbol S. Valence II, also IV, VI. Atomic weight 82. Density 82. Molecular weight 64. Specific gravity about 2. Melting-point 114.5°.

Occurrence.—Sulfur occurs free in considerable quantities in volcanic regions. Large deposits are found in Italy, Sicily, China, India, Iceland, California, in the vicinity of Lake Superior, and in the Yellowstone Park region. The sulfur may be imbedded in or interstratified with clay, earth, and stone, or it may lie in the so-called *living beds* where the deposit is continuously growing because of the separation of sulfur by chemical processes.

Sulfur occurs in nature in numerous compounds, chief of which are the sulfids of the heavy metals and the sulfates of the alkali and earth metals (Groups I and II). These constitute important native minerals, of which the following are examples:

Sulfids.—Iron pyrites FeS_2, copper pyrites $CuFeS_2$, galena PbS, blend ZnS, cinnabar HgS, antimonite Sb_2S_3, realgar As_2S_2, orpiment As_2S_3.

Sulfates.—Heavy spar $BaSO_4$, gypsum $CaSO_4,2H_2O$, epsom salts $MgSO_4,7H_2O$, glauber salts $Na_2SO_4,10H_2O$, copperas $FeSO_4,7H_2O$.

Sulfur is an essential constituent of plant and animal bodies, and the unpleasant odor of decaying organic matters is largely due to the sulfur compounds formed in the decomposition.

History.—Sulfur has been known from the earliest times.

The name is from the Latin. It was formerly called *brimstone* from the old English *brenston,* which means *burn-stone,* referring to its combustibility.

Preparation.—Sulfur may be obtained in the following ways:

1. By the action of hydrogen sulfid upon sulfurous oxid:

$$2H_2S + SO_2 = 2H_2O + 3S.$$

It is by this reaction and similar ones that the sulfur has been deposited in volcanic regions, as these two gases are always found in the exhalations from volcanic vents.

2. By the incomplete combustion of hydrogen sulfid:

$$H_2S + O = H_2O + S.$$

This reaction is better represented in two stages, the sulfurous oxid formed in the first acting upon the hydrogen sulfid to set sulfur free in the second:

$a.$ $H_2S + 3O = H_2O + SO_2$, . $b.$ $2H_2S + SO_2 = 2H_2O + 3S.$

3. By heating metallic sulfids such as iron pyrites:

$$2FeS_2 = Fe_2S_3' + S.$$
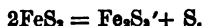
4. By decomposition of sulfur compounds with acids.

5. By separating the free sulfur as it is found native or in the waste products of manufacture from the substances with which it is mixed by fusion or distillation.

There are three principal sources of commercial sulfur:

1. *Native sulfur.* The sulfur-bearing rock is gathered into kilns usually made on a hillside and with a sloping bottom. The kiln is covered over with burnt-out ore so as to limit the combustion. The heap is first lighted with wood and then the heat continued by the burning of a portion of the sulfur. The melted sulfur is drawn off below into moulds. About one third of the sulfur is lost in the operation.

2. *The alkali waste of the soda manufacture.* In the Leblanc soda process the residue in the lixiviating vats contains, along with the lime, calcium sulfid and alkali sulfids. On blowing a current of air through the mixture, complicated chemical changes take place whereby there are formed calcium hydrosulfid, CaH_2S_2, calcium polysulfids, as CaS_5, and calcium thiosulfate, CaS_2O_3. On

treating this mixture with hydrochloric acid sulfur is set free. The following equation may be taken to represent the reaction:

$$CaH_2S_2 + 2CaS_5 + 2CaS_2O_3 + 10HCl = 5CaCl_2 + 6H_2O + 16S.$$
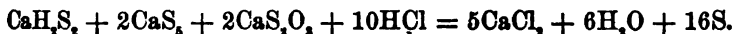
3. *The spent iron oxid of gas-works.* The hydrated iron oxid used in the purifiers absorbs the hydrogen sulfid thus:

$$Fe_2H_6O_6 + 3H_2S = 2FeS + 6H_2O + S.$$
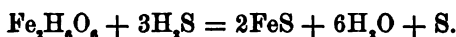
When the material no longer absorbs the gas it is thrown out and exposed to air and moisture by which the ferrous sulfid is reoxidized with the separation of sulfur:

$$2FeS + 3H_2O + 3O = Fe_2H_6O_6 + 2S.$$
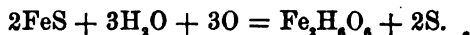
The material is now used again and the operation repeated until it contains about 50 per cent of sulfur, when it ceases to be effective in the absorption of hydrogen sulfid. The sulfur is obtained from this mixture by distillation.

Purification.—The crude sulfur obtained by the commercial methods is purified by distillation. The sulfur is melted in a pot by the waste heat of the fire and conducted through a pipe to the retort below, where it is converted into vapor. The vapor passes into a brick chamber and at first condenses on the walls in the fine crystalline powder called *flowers of sulfur*, which is swept down and removed. The walls presently become hot and the sulfur melts and collects on the floor. It is drawn off from time to time into a vessel from which it is ladled into cylindrical wooden moulds. This is the *roll sulfur* of commerce.

Illustrations.—To illustrate the separation of sulfur (*a*) fill two cylinders, the one with hydrogen sulfid and the other with sulfurous oxid, bring them mouth to mouth and let the gases mix. The hydrogen sulfid cylinder should be twice as large as the other. (*b*) Heat in a test-tube some finely pulverized iron pyrites. The sulfur condenses on the wall of the tube.

Physical Properties.—Sulfur in the ordinary form is a pale yellow, brittle, crystalline solid of specific gravity 2.05. When warmed in the hand or by application of heat it gives out a crackling noise caused by the movement of the crystals, and when repeatedly warmed it falls to pieces. It is a bad conductor of heat

and electricity, and when rubbed becomes negatively electrified. It is insoluble in water, dissolves with difficulty in ether and alcohol, but is readily soluble in carbon disulfid, sulfur chlorid, petroleum, benzine, turpentine, and other hydrocarbons. The best solvent is carbon disulfid, 100 parts of which dissolve 46 parts of sulfur.

Sulfur is tasteless because it is insoluble, and odorless because it is not volatile at the ordinary temperature. The odor which is usually perceived is due to various sulfur compounds which may be present. It melts at 114.5° to a yellow, mobile liquid of specific gravity 1.803. On being further heated, the liquid darkens and thickens until at 230° it is almost black and so viscid that it will not pour from the vessel. Above 300° it becomes limpid again, retaining, however, its dark color, and at 448° it boils, yielding a pâle yellow vapor. The vapor density at 1000° is 32, corresponding to a molecular formula S_2. As the temperature falls the density rises and at boiling-point indicates the formula S_8. This formula is also obtained by the study of sulfur solutions.

There are four physical forms of sulfur, at least three of which seem to be true allotropic modifications.
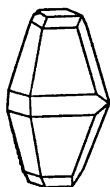
α. *Rhombic or Octahedral Sulfur.*—This is the native and the ordinary form and has the properties which have just been given as belonging to sulfur. In native sulfur large transparent rhombic octahedrons are often found. Similar crystals are obtained by slow cooling of sulfur vapor, or by the evaporation of solutions, or by allowing melted sulfur to crystallize at 90°.

β. *Monoclinic or Prismatic Sulfur.*—When melted sulfur is allowed to cool in the air it crystallizes in long needle-shaped monoclinic prisms. These may be shown by pouring off the liquid after a few crystals have been formed in a vessel of cooling sulfur. The rhombic form becomes monoclinic between 100° and 114°. When a crystal of rhombic sulfur is kept at this temperature for some time it becomes opaque owing to the formation of numerous small monoclinic crystals.
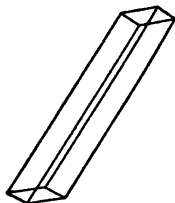
FIG. 60.

Monoclinic sulfur has a specific gravity 1.96 and melts at 120°. It dissolves in carbon disulfid, but crystallizes from the solution in

the rhombic form. It is unstable, becoming opaque in a few hours and in a day or two changing completely to the rhombic form. This change is accelerated by vibration, or by scratching the crystals, or by the action of sunlight, and is accompanied by the evolution of heat to the amount of 73 calories for each gram-atomic weight of sulfur.

γ. White Amorphous Sulfur.—Flowers of sulfur consists of very small particles of rhombic sulfur mixed with a varying quantity of white amorphous sulfur. This latter is obtained by treating flowers of sulfur with carbon disulfid, which removes the rhombic variety and leaves the amorphous substance undissolved. It is also produced when intense light, such as the sun or electric light, acts upon sulfur in solution in carbon disulfid. The clear liquid soon becomes turbid from the separation of amorphous sulfur.

This form of sulfur is a white, amorphous powder insoluble in carbon disulfid. It remains unchanged at the ordinary temperature, but at 100° it turns yellow and passes into the soluble rhombic form with evolution of heat.

δ. Plastic Sulfur.—When sulfur in its state of viscid fusion is suddenly cooled, or when in limpid fusion at a higher temperature, it is poured slowly into cold water, it becomes a semi-solid, tough, elastic mass which can be drawn into threads, moulded into various forms, and impressed with seals. This is called *plastic sulfur*. It has a dark amber color, is semi-transparent, has a specific gravity 1.95, and is insoluble in carbon disulfid. It gradually passes back to the rhombic form and the change takes place quickly at 100°.

Sulfur comes into commerce in the three following forms:

1. *Roll Sulfur* or *Brimstone*, the alpha variety already described.

2. *Flowers of Sulfur*, which we have found to be a mixture of rhombic and amorphous sulfur.

3. *Milk of Sulfur* (Lac sulfur), a fine sulfur powder obtained by precipitating sulfur from a solution of polysulfids by means of hydrochloric acid. When sulfur, lime, and water are boiled together, soluble polysulfids of calcium are formed, mainly the pentasulfid. If to the clear liquid which may be decanted or

siphoned off hydrochloric acid be added, the sulfur is precipitated:

$$CaS_5 + 2HCl = CaCl_2 + H_2S + 4S.$$

This product is amorphous, pale yellow, and soluble in carbon disulfid. It is probably simply finely divided ordinary sulfur.

Illustrations.—Common roll sulfur and flowers of sulfur are examples of the rhombic form. Dissolve one half a gram in 3 cc. of carbon disulfid, let evaporate and examine the small rhombic crystals.

To prepare the prismatic form heat in a deep evaporating-dish some 50 grams of sulfur nearly to boiling. Allow to cool slowly and as soon as the crystals have well begun to form pour off the excess of liquid sulfur, breaking the crust if necessary. The dish will be found covered with the needle-shaped crystals.

Treat flowers of sulfur with carbon disulfid, filter and wash with carbon disulfid. The residue is amorphous sulfur.

To show the fusion peculiarities of sulfur and the formation of the plastic variety melt in a wide test-tube 30 grams of roll sulfur with constant shaking. The liquid is first mobile, then becomes viscid, when the tube may be inverted. When it has nearly reached the boiling-point pour in a fine stream into a beaker of water. Preserve the plastic mass and note that in a few days it becomes brittle and yellow.

Chemical Properties.—At the ordinary temperature sulfur is inert, but with the aid of heat and in the nascent state it is one of the most active of the chemical elements. It ignites at 260° and burns with a pale-blue flame to SO_2. In oxygen the flame is brighter and with the SO_2 a small quantity of SO_3 is formed. When burned under pressure a still larger quantity of SO_3 is produced. At 180° slow oxidation takes place with phosphorescence, and even at the ordinary temperature in the presence of air and moisture it is slowly converted into sulfuric acid. Boiling nitric and sulfuric acids dissolve sulfur, the first oxidizing it to sulfuric acid and the second to sulfurous oxid, SO_2. It is most readily oxidized by heating it with a mixture of nitric acid and potassium chlorate. Hot alkalies dissolve it, yielding a mixture of sulfids and hyposulfites.

By the aid of heat sulfur may be made to combine with nearly all of the elements negative and positive. Several of the metals burn in its vapor. It unites readily with hydrogen, oxygen, and hydroxyl.

In its chemical actions it closely resembles oxygen and forms many similar compounds, both binaries and ternaries. Corresponding compounds of oxygen and sulfur give similar chemical actions:

$$2NaHO + H_2SO_4 = Na_2SO_4 + H_2O.$$
$$2NaHS + H_2SO_4 = Na_2SO_4 + H_2S.$$
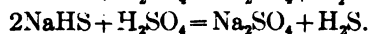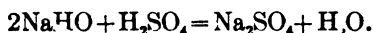
Illustrations.—Ignite some sulfur and note the flame and the odor, which is that of the SO_2 produced.

The direct union of sulfur with other elements may be shown as follows: Heat sulfur in a small flask until it boils and the flask is full of the vapor. Lower successively into the flask a jet of hydrogen, a bit of sodium, a copper ribbon, a bundle of red-hot steel wire. They all burn to sulfids. If a white-hot bar of iron be touched to a stick of roll sulfur, the iron and sulfur combine and there falls a brilliant shower of the molten sulfid.

To show the spontaneous oxidation of sulfur stir together flowers of sulfur and water for a few minutes and filter. The liquid contains sulfuric acid, as is shown by its reddening litmus and giving with barium chlorid a precipitate of barium sulfate.

Physiological Properties.—Sulfur is not poisonous. Taken in small quantities it is medicinal, but in large quantities it is injurious to the human body. It and several of its compounds are much used in skin-diseases.

Tests.—Sulfur is recognized by its general physical properties and its odor when burned. To detect it in its compounds fuse with sodium carbonate, moisten, and place on a piece of silver. A dark spot of silver sulfid is formed.

Uses.—Sulfur is used in the manufacture of sulfuric acid, gunpowder, vulcanized or hardened rubber, sulfur matches, and various sulfids. It also serves as a medicine and for many minor purposes in the arts.

SULFUR COMPOUNDS.

Sulfur is chemically active and its compounds are very numerous. It unites with nearly all the elements both positive and negative. It performs the linking function like oxygen and yields similar compounds, sulfids, thioacids, thiobases, and thiosalts. It forms the colorless, active, negative sulfid ion S'', but like oxygen more readily enters into complex ions such as HS', SO_4'', CS_3'', etc. The heat of formation of the sulfid ion is $-8,400$ calories.

COMPOUNDS OF SULFUR WITH HYDROGEN.

Sulfur forms two compounds with hydrogen corresponding to the two oxids of hydrogen:

Hydrogen sulfid, H_2S,   or   H—S—H.   Gas.
Hydrogen persulfid, H_2S_2,   or   H—S—S—H.   Liquid.

In the first sulfur is bivalent and stands between the hydrogen atoms. In the second sulfur seems to have a valence one (pseudomonad), but there are good reasons for believing that it is the monovalent radical (HS)′, called *hydrosulfuryl*, existing free by uniting with another similar radical, thus: $(HS)_2$.

HYDROGEN SULFID.

Formula H_2S. Molecular weight 34. Density 17. Liter weighs 1.52.

History and Occurrence.—Hydrogen sulfid was discovered by Scheele in 1777. It occurs in volcanic gases, being formed by the direct union of its elements. It is found in small quantities in the atmosphere, since it is formed by the decomposition of organic matters which contain sulfur. It is produced by the union of hydrogen and sulfur in the dry distillation of coal and hence is found in coal-gas. It is the characteristic constituent of sulfur waters and gives them their odor and medicinal properties. Liquid hydrogen sulfid was first prepared by Faraday in 1823.

Preparation.—Hydrogen sulfid is formed in the following ways:

1. By the direct union of the elements, as when sulfur vapor and hydrogen are passed together through a red-hot tube, or when hydrogen is passed through boiling sulfur, or over hot metallic sulfids.

2. By the action of nascent hydrogen upon sulfur, as in the decomposition of organic matter containing sulfur, in the distillation of coal, and when sulfur is heated with certain organic compounds such as paraffin.

3. In the reduction of alkaline sulfates by decaying organic matter.

4. By the action of acids upon sulfids: $FeS + H_2SO_4 = FeSO_4 + H_2S$.

Hydrogen sulfid is commonly prepared according to the last method. Fragments of iron sulfid are placed in a bottle which is furnished with safety- and delivery-tubes and the acid added through the safety-funnel. The gas is collected by displacement, or is conducted into water to form the solution, or it may be burned from a jet like hydrogen. Sulfuric acid of proper strength has a specific gravity 1.1 and contains 15 per cent H_2SO_4.

Physical Properties.—Hydrogen sulfid is a colorless gas with a sweetish taste and an unpleasant odor recalling that of rotten eggs and putrefying animal matters. It is a little heavier than air, its specific gravity being 1.177. Water dissolves at 0° 4.37 volumes of hydrogen sulfid; at 5° 4.18 volumes; at 10° 3.58 volumes; at 15° 3.23 volumes; and at 20° 2.9 volumes. At 100° the gas is wholly expelled from solution. The solution has the properties, odor, and taste of the gas.

Under a pressure of 17 atmospheres at the ordinary temperature, or at − 70° under atmospheric pressure, hydrogen sulfid condenses to a colorless liquid which boils at − 61.8° and has a specific gravity 0.9. At low temperatures it becomes a white crystalline solid which melts at − 85°. Its critical temperature and pressure are 100° and 92 atmospheres.

Chemical Properties.—Hydrogen sulfid burns with a pale-blue flame to sulfurous oxid and water: $2H_2S + 3O_2 = 2SO_2 + 2H_2O$. If the supply of oxygen is deficient, sulfur separates: $2H_2S + 2O_2 = SO_2 + 2H_2O + S$. A mixture of two volumes of hydrogen sulfid with three volumes of oxygen explodes when ignited. It is unstable, as might be expected from its low heat of formation, which is as follows:

$(H_2, S, gas) = 2700$ cal. $(H_2S, Aq) = 4600$ cal. $(H_2, S, Aq) = 7300$ cal.

Hydrogen sulfid is decomposed by oxygen and the halogens, these elements taking the hydrogen and setting the sulfur free:

$$H_2S + O = H_2O + S; \quad H_2S + Cl_2 = 2HCl + S.$$
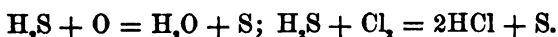
Hydrogen sulfid water soon becomes turbid because of this separation of sulfur. The action with fluorin, chlorin, and bromin is exothermic and takes place at the ordinary temperature, while that with iodin is endothermic and must be aided by heat unless water be present, in which case the solution of the hydrogen iodid is sufficient to keep up the action. Because of its action with oxygen hydrogen sulfid is a rather powerful reducing agent. It reduces acids such as chromic, manganic, nitric, and sulfuric: $H_2SO_4 + H_2S = SO_2 + 2H_2O + S$. If fuming nitric acid be poured into a jar of the dried gas, ignition takes place with a slight explosion. It dissociates at red heat, $H_2S \rightleftarrows H_2 + S$.

Hydrogen sulfid is chemically active for three reasons: first

because it is unstable, second because it always contains free active ions, third because both hydrogen and sulfur have strong affinities. The solution is more active than the gas because the dissociation is greater. There are two sets of ions, as follows:

$$H_2S = \overset{+}{H'} + \overset{+}{H'} + \overset{-}{S''} \quad \text{and} \quad H_2S = \overset{+}{H'} + H\overset{-}{S'}.$$
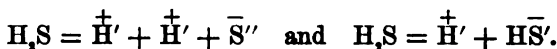
There will, therefore, be two kinds of reactions, the one forming sulfids and the other hydrosulfids. The former is the more common. These reactions are characteristic and occur with the metals and their oxids, hydroxids, and salts. Examples are:

$$Pb + H_2S = PbS + H_2; \quad CuO + H_2S = CuS + H_2O;$$
$$CaH_2O_2 + 2H_2S = CaH_2S_2 + 2H_2O; \quad FeSO_4 + H_2S = FeS + H_2SO_4.$$
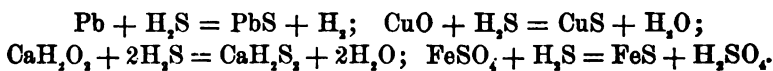
Hydrogen sulfid thus appears as a weak binary acid resembling the haloid acids. It has a structure similar to that of water and bears the same relation to the thioacids, thiobases, and thiosalts that water does to the ordinary acids, bases, and salts:

H—S—H, hydrogen sulfid;   H—O—H, water.

K—S—H, potassium hydrosulfid; K—O—H, potassium hydroxid.
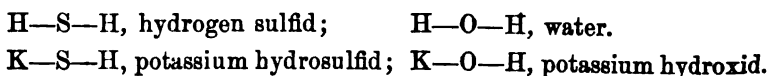
It is because of the action of atmospheric hydrogen sulfid upon metals that articles made of tin, lead, silver, etc., tarnish in the air, and that white-lead paint darkens with age, most of the metallic sulfids being black. Eggs are rich in sulfur compounds and hence blacken and injure silver spoons.

Illustrations.—The solution of hydrogen sulfid is obtained by allowing it to bubble through water. The gas may be liquefied by generating it in a closed tube.

Burn hydrogen sulfid from a jet. Fill a jar and bring a burning match to its mouth. Note the flame and the deposit of sulfur. Fill a jar with a mixture of the gas and oxygen or air and ignite.

Bring together the mouths of two jars filled the one with chlorin and the other with moist hydrogen sulfid. As the action goes on sulfur is deposited on the wall of the jar.

To show the action of hydrogen sulfid upon metals pass the gas successively into cylinders containing the following solutions: copper sulfate, lead nitrate, cadmium chlorid, antimonous chlorid, and zinc sulfate. A clear solution of antimonous chlorid is obtained by adding a little tartaric acid, and the zinc sulphate must be made alkaline with ammonia.

Physiological Properties.—Hydrogen sulfid is quite poisonous. When breathed for some time even very dilute, it causes headache, dizziness, stupor, and finally asphyxia. Its effects are more marked upon some animals than upon others. Cold-blooded animals are least affected. One part in 1500 of air is fatal to birds, one in 800 to dogs, and one in 200 to rabbits. The best antidote is very dilute chlorin, which may be obtained by moistening a cloth with acetic acid and sprinkling over it bleaching-powder. The solution when taken into the stomach in moderate quantities is medicinal; but when too much is used it produces derangement.

Tests.—Hydrogen sulfid is recognized by its odor and its action with metals and their salts. Paper moistened with solution of lead acetate is turned brown or black by it.

Uses.—Native waters which have hydrogen sulfid in solution are much used as medicinal mineral waters. They are considered beneficial in certain ailments such as diseases of the skin, liver, and kidneys. The artificial gas and solution are extensively used as reagents in analytical chemical laboratories in the separation and identification of metals.

Hydrosulfids.—Hydrosulfids are analogous to the hydroxids and may be derived by replacing one H of hydrogen sulfid, as K—S—H. They are unstable and only a few are known.

Sulfids.—Sulfids may be regarded as binary compounds of sulfur. or as derivatives of H_2S, both hydrogen atoms being replaced:

$$H—S—H, \quad K—S—K, \quad K—S—Na, \quad Ba = S, \quad Cl—S—Cl.$$
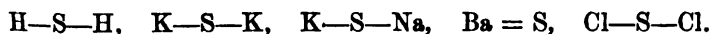
A few sulfids are gases, some are liquids, the rest are solids. They all dissolve in acids, while only the sulfids of the alkalies and of hydrogen are soluble in water. They closely resemble the oxids in many respects. Positive and negative sulfids unite to form thiosalts, $K_2S + SnS_2 = K_2SnS_3$. Compare $K_2O + CO_2 = K_2CO_3$. With acids they give hydrogen sulfid and a salt of the acid: $FeS + H_2SO_4 = FeSO_4 + H_2S$. Negative sulfids are decomposed by water yielding hydrogen sulfid and an acid, $P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S$.

Sulfids are formed by the direct union of the elements, or by

the action of hydrogen sulfid or ammonium sulfid upon metals or metallic salts:

$$Cu + S = CuS, \quad Fe + H_2S = FeS + H_2,$$
$$H_2S + ZnSO_4 = H_2SO_4 + ZnS.$$
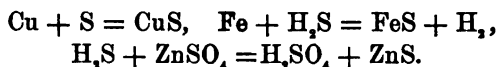
Sulfids may be classified according to their solubility as follows:

1. Sulfids insoluble in dilute acids and precipitated from acid solution by hydrogen sulfid; as, HgS, PbS, Bi_2S_3, CuS, CdS, Sb_2S_3, As_2S_3, SnS, AuS, PtS_2.

2. Sulfids insoluble in alkaline solution and precipitated by H_2S in the presence of ammonia ; as, FeS, NiS, CoS, MnS, ZnS.

3. Sulfids soluble in water and not precipitated by H_2S; as, BaS, SrS, CaS, Na_2S, K_2S.

Some sulfids may be recognized by their characteristic colors. Zinc sulfid is white, arsenous sulfid pale yellow, antimonous sulfid reddish yellow, and cadmium sulfid golden yellow.

HYDROGEN PERSULFID.

Formula H_2S_2. Molecular weight 66. Density 33. Specific gravity 1.73.   ♪

History and Occurrence.—Hydrogen persulfid was first discovered by Scheele and afterwards investigated by Berthelot, Thénard, and Hofmann. It does not occur in nature.

Preparation.—As hydrogen peroxid is formed by the action of acids upon peroxids, so hydrogen persulfid is obtained from persulfids by similar action:

$$CaS_2 + 2HCl = CaCl_2 + H_2S_2.$$
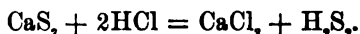
It may also be obtained as follows: When hydrogen sulfid acts upon strychnine, a beautiful crystalline compound results having the formula: $2C_{21}H_{22}N_2O_2,3H_2S_2$. From this the H_2S_2 is separated by the action of acids.

Illustrations.—To prepare hydrogen persulfid pour into dilute hydrochloric acid with constant stirring a solution of calcium persulfid obtained by boiling together one part of lime, two parts of flowers of sulfur, and sixteen parts of water. The oily liquid settles to the bottom and may be removed with a pipet or by means of a separatory funnel.

The solution of calcium persulfid contains also calcium polysulfids and sulfur is set free as follows : $CaS_4 + 2HCl = CaCl_2 + H_2S_2 + 3S$.

Physical Properties.—Hydrogen persulfid is a yellow, oily liquid of specific gravity 1.73. It has an acrid, sweetish-bitter

taste and a pungent, irritating odor accompanied by the odor of hydrogen sulfid. The vapor attacks the eyes and mucous membranes and the liquid blisters the skin. It is poisonous like hydrogen sulfid. It is insoluble in water, but soluble in carbon disulfid and ether. It dissolves sulfur freely, and since sulfur is set free in its preparation and in its decomposition, it can scarcely be obtained free from this element. Indeed, it probably unites to sulfur in several proportions so that we may have the series of compounds, H_2S, H_2S_2, H_2S_3, H_2S_4, H_2S_5.

Chemical Properties.—Hydrogen persulfid is unstable, decomposing gradually at the ordinary temperature and in the presence of moisture, and rapidly when heated. When quite dry it is more stable. It is chemically active, a vigorous reducing agent, and bleaches feebly. It dissolves phosphorous and iodin slowly, forming P_2S_3 and HI. It is not acted upon by SO_2. It is simply of scientific interest, having no commercial importance.

COMPOUNDS OF SULFUR WITH THE HALOGENS.

Sulfur has but little affinity for the halogens and all the compounds are unstable. The following have been prepared:

$$SF_6, \quad S_2Cl_2, \quad SCl_2, \quad SCl_4, \quad S_2Br_2, \quad S_2I_2, \quad SI_2.$$

The most stable of these compounds is S_2Cl_2, and it is the only one which can be gasified without decomposition. SCl_4 can only be formed and kept below $-20°$.

Sulfur Hexafluorid, SF_6, formed by direct union of the elements, is a gas which on exposure to cold becomes a white crystalline solid. It melts at $-55°$ and boils at about the same temperature. It is remarkable for being very stable and chemically inactive and for having neither odor nor taste.

Disulfur Dichlorid (Sulfur monochlorid), S_2Cl_2.—*Preparation.* —This substance is prepared by passing dry chlorin over heated sulfur. The distillate is redistilled to separate it from the sulfur dichlorid which is formed at the same time. It is also produced by distilling sulfur with stannous chlorid, $SnCl_2$, or mercuric chlorid, $HgCl_2$, or phosphoric chlorid, PCl_5.

Physical Properties.—Disulfur dichlorid is a dark-yellow, oily, fuming liquid with a disagreeable, penetrating odor and an acid taste. It has a specific gravity 1.7, boils at 138°, and does not solidify at $-75°$. The density of the vapor is 67.4. This indi-

cates a molecular weight of 134.8, and corresponds to the formula S_2Cl_2, which has probably the structure Cl—S—S—Cl. From its analogy to thionyl chlorid, $O = S{<}^{Cl}_{Cl}$, its formula may be written $S^{II}S^{IV}Cl_2$, or $S = S{<}^{Cl}_{Cl}$, in which one S is bivalent and the other tetravalent. It is therefore sometimes called *sulfothionyl chlorid.* It is soluble in carbon disulfid, benzene, alcohol, and ether, making solutions all more or less unstable. It dissolves sulfur in such quantity that the solution is a syrupy liquid containing as much as 66 per cent of sulfur. This solution dissolved in carbon disulfid is used in vulcanizing India rubber.

Chemical Properties.—Disulfur dichlorid is the most stable of the halogen compounds of sulfur, and yet it is readily decomposed by numerous chemical agents. With water it yields hydrochloric acid, sulfurous oxid, and sulfur, with hydrogen sulfid it gives hydrochloric acid and sulfur, and it unites with ammonia to form the compound $S_2Cl_2,4NH_3$.

The vapor attacks the mucous membranes, irritates the eyes, causing tears, and produces other physiological effects similar to those of chlorin.

Sulfur Dichlorid (Hyposulfurous chlorid), SCl_2.—This compound is prepared by passing dry chlorin into disulfur dichlorid at 0° until the liquid assumes a deep-red color and removing the excess of chlorin with a stream of carbon dioxid. To preserve it the vessel should be kept full of chlorin and away from the light.

Sulfur dichlorid is a brownish-red liquid with odor, taste, and physiological properties like S_2Cl_2. It has a specific gravity 1.65 and has no constant boiling-point. It is decomposed by heat and light and various chemical agents. Above 6° it begins to separate into S_2Cl_2 and Cl_2, at 86° the dissociation is 50 per cent, and at 130° it is complete. With water it gives HCl and $H_2S_2O_3$, and with ammonia N, S, NH_4Cl. Recent investigations show that this compound is probably a mixture of S_2Cl_2 and SCl_4.

Sulfur Tetrachlorid (Sulfurous chlorid), SCl_4.—Sulfur tetrachlorid is prepared by passing dry chlorin into S_2Cl_2 at —22° until it is saturated. It is a brownish-yellow liquid which decomposes rapidly as the temperature rises. At —15° the dissociation amounts to 58 per cent and at 7° it is complete. It acts vigorously with water, giving HCl and SO_2. It forms molecular compounds with metallic chlorids and iodin trichlorid such as $AuCl_3$, SCl_4, and ICl_3, SCl_4.

Disulfur Dibromid, S_2Br_2, is prepared by dissolving sulfur in bromine and removing the excess of bromin with a stream of dry carbon dioxid. It is a ruby-red liquid which boils between 190° and 200°, with decomposition.

Disulfur Diiodid, S_2I_2, is formed by heating iodin and sulfur together, or by the action of ethyl iodid upon disulfur dichlorid:

$$2C_2H_5I + S_2Cl_2 = 2C_2H_5Cl + S_2I_2.$$
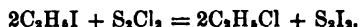
It is a solid which forms lustrous tabular crystals and melts at 60°.

Sulfur Hexaiodid, SI_6.—When a solution of iodin and sulfur in slight excess in carbon disulfid is allowed to evaporate at a low temperature, a gray crystalline substance separates, which is said to have the formula SI_6. It is isomorphic with iodin, and on exposure to air slowly decomposes, the iodia evaporating and leaving the sulfur.

<div align="center">

OXIDS OF SULFUR.

</div>

The valence of sulfur being II, IV, and VI, there should be three oxids: Hyposulphurous oxid, SO or S=O; sulfurous oxid, SO_2 or O=S=O; and sulfuric oxid, SO_3, or O=S=O. The

<div align="center">

$\overset{\|}{O}$

</div>

first has not been obtained, although the corresponding acid and its salts are well known. The other two are easily prepared.

Besides these there are two other oxids of sulfur whose structure is not so apparent. In them the sulfur seems to have valences III and VII, but the formulas may be written so as to preserve the artiad character of the element:

Sulfur sesquioxid,
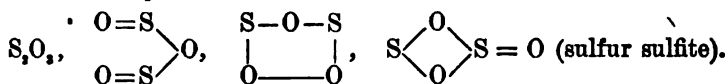
Sulfur peroxid,

<div align="center">
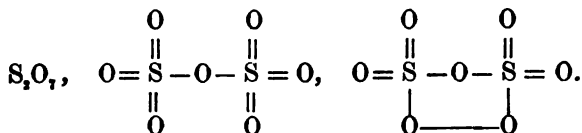
SULFUROUS OXID (SULFUR DIOXID).

</div>

Formula SO_2. Molecular weight 64. Density 32. Liter weighs 2.87 grams.

Occurrence.—Sulfurous oxid occurs in volcanic gases and in the waters of certain volcanic regions. It is produced in considerable

quantity in cities from the sulfur found in coal, but is quickly oxidized to sulfuric acid, so that the air contains only traces of it.

History.—Sulfurous oxid has been known from remote times, since it is produced by burning sulfur. It is mentioned by many ancient writers, and its disinfecting powers were known to the Romans. It was long supposed to be identical with sulfuric acid until Stahl proved it to be a distinct substance. In 1775 Priestley separated and collected the pure gas.

Preparation.—Sulfurous oxid is prepared:

1. By burning sulfur or sulfur compounds in air or oxygen :

$$S + O_2 = SO_2; \quad H_2S + 3O = H_2O + SO_2.$$
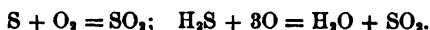
2. By the decomposition of sulfuric acid when it is heated with carbon or sulfur or metals such as copper, silver, mercury, and zinc :

$$C + 2H_2SO_4 = 2H_2O + CO_2 + 2SO_2.$$
$$S + 2H_2SO_4 = 2H_2O + 3SO_2.$$
$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$
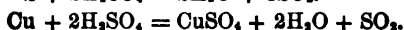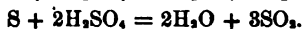
3. By the action of acids upon sulfites :

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2.$$
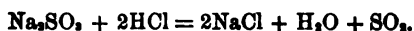
4. By heating sulfur with the oxids of lead, mercury, manganese, zinc, etc.:

$$2PbO + 3S = 2PbS + SO_2.$$

When sulfurous oxid is prepared by burning sulfur, a little SO_3 is formed at the same time and this makes the gas cloudy. ·

For laboratory purposes sulfurous oxid is most conveniently prepared as follows: Place bits of copper in a flask furnished with safety- and delivery-tubes, add enough sulfuric acid to nearly cover the copper and heat. When the gas begins to come off, the lamp should be removed or the action will be too violent. The gas is collected by displacement of air or over mercury.

Physical Properties.—Sulfurous oxid is a colorless gas with a sour taste and the familiar suffocating odor of burning sulfur. Its specific gravity is 2.22. It dissolves readily in water to form sulfurous acid: $SO_2 + H_2O = H_2SO_3$. The quantity of the gas absorbed depends upon the temperature and pressure, and the solution increases in volume as it increases in strength. This is illustrated in the following table:

Temperature.	1 Vol. Water dissolves SO_2.	1 Vol. of Solution contains SO_2.
0°	79.79 vols.	68.81 vols.
20°	39.37 "	36.21 "
40°	18.77 "	17.01 "
100°	0	0

Above 40° the quantity dissolved varies as the partial pressure of the gas.   The heat of solution is 7700 cal.

Under a pressure of one and a half atmospheres at 0° or at — 10° under ordinary pressure sulfurous oxid condenses to a colorless mobile liquid of specific gravity 1.45, which boils at — 8° and becomes a white crystalline solid at — 76°. Its critical temperature is 155.4° and its critical pressure is 78.9 atmospheres.   The vapor tension at — 10° is 762 mm. and at 0° is 1165 mm. of mercury.   When the liquid is placed in vacuo its temperature sinks to — 76° and it freezes by its own evaporation.   The heat of vaporization at 0° is 91.2 cal.

Illustrations.—The solubility of sulfurous oxid may be shown by inverting a cylinder of the gas over water, The water rises as the gas dissolves.

To obtain liquid sulfurous oxid let the gas pass through sulfuric acid to dry it and then into a U tube which is surrounded by a mixture of ice and salt. It may be kept in sealed glass tubes or in strong tubes with close-fitting stop-cocks.

To show the great cold produced by its evaporation pour some of the liquid upon a small globule of mercury in a clay crucible and blow over it a current of air: the mercury is frozen. Pour some of the liquid on a little water in a dish: the water is frozen.

Chemical Properties.—Sulfurous oxid acts vigorously with numerous chemical compounds.   Although it does not burn and does not support ordinary combustion, it is still both an oxidizing and a reducing agent.   Metals such as potassium, tin, and iron burn when heated in it to sulfids and oxids, and it unites directly to the metallic oxids and peroxids to form sulfids and sulfates, and with chlorin to form sulfuryl chlorid, SO_2Cl_2. It is reduced by hydrogen sulfid, hydrogen phosphid, and the haloid acids in the presence of moisture.   It reduces water in the presence of the halogens, forming the haloid acid and sulfuric acid:

$$SO_2 + 2H_2O + Cl_2 = 2HCl + H_2SO_4.$$
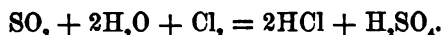
In the case of iodin, unless the acid is kept very dilute, the reverse action takes place:

$$H_2SO_4 + 2HI = 2H_2O + I_2 + SO_2.$$
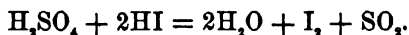
It bleaches because of its reducing action, takes oxygen from water, becoming SO_3 and then H_2SO_4, and the nascent hydrogen reduces the coloring matter by taking its oxygen. It sometimes seems to unite with the coloring matter, and the color is restored by alkalies and weak acids. In most cases the bleaching is temporary and the color gradually returns.

Sulfurous oxid is decomposed by bright light, by the electric spark, and by being heated to $1200°$: $3SO_2 = 2SO_3 + S$. If a beam of electric light be passed through a tube of the gas, it becomes cloudy in a few minutes because of this decomposition. When the tube is removed from the light, the SO_2 is re-formed and the cloud disappears.

The formation of sulfurous oxid is strongly exothermic, as is indicated by the thermal equations:

$$(S, O_2) = 71,000 \text{ cal. } (SO_2, Aq) = 7,700 \text{ cal. } (S, O_2, Aq) = 78,700 \text{ cal.}$$
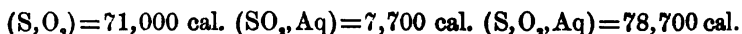
Illustrations.—The reducing action of sulfurous oxid may be shown by passing it through an infusion of purple cabbage, rose-leaves, or litmus. The color is discharged, but is restored by adding sulfuric acid. It also decolorizes a solution of potassium permanganate.

To show the oxidizing action pass the gas through a tube containing a little reduced iron or a piece of sodium. Gently warm the tube, and the metal burns in the gas.

To show its union with peroxids pass the gas over some lead peroxid in a tube, or sprinkle sodium peroxid in a jar of the gas.

Physiological Properties.—Sulfurous oxid is a stifling, poisonous gas which can be breathed only in the smallest quantities. It is a bactericide and antiseptic. The solution taken internally has medicinal effects.

Tests.—Sulfurous oxid is recognized by its odor and by its turning paper blue which has been moistened with a solution of potassium-iodate and starch:

$$2KIO_3 + 4H_2O + 5SO_2 = 5K_2SO_4 + 4H_2SO_4 + I_2.$$
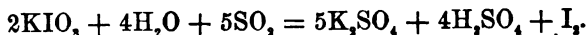
Uses.—Sulfurous oxid is used in many manufactures, especially for sulfuric acid, sulfates, and sulfites. It is employed for bleaching materials which are injured by chlorin, such as straw, silk, wool, and sponge. It is used as a reducing agent in laboratories, as a preservative of fruits and vegetables, and as a disinfectant. As a preservative it is neither good nor wholesome.

SULFURIC OXID (SULFUR TRIOXID).

Formula SO_3. Molecular weight 80. Density 40. Specific gravity 1.94 at 16°.

Preparation.—Sulfuric oxid may be prepared in the following ways:

1. By the action of oxygen and oxidizing agents upon sulfurous oxid:

$$SO_2 + O = SO_3; \quad SO_2 + NO_2 = SO_3 + NO.$$
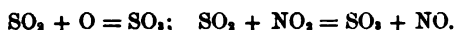
2. By heating disulfuric acid and disulfates:

$$H_2S_2O_7 = H_2SO_4 + SO_3; \quad Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

3. By the action of phosphorus pentoxid upon sulfuric acid:

$$P_2O_5 + H_2SO_4 = 2HPO_3 + SO_3.$$
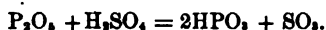
In the laboratory sulfuric oxid may be conveniently prepared by heating disulfuric acid and conducting the vapors into a well cooled and perfectly dry receiver.

It is also obtained by passing a mixture of oxygen and dry sulfurous oxid through a hot tube containing platinum sponge or platinized asbestus, and condensing the oxid in a dry receiver. This method is commercial. The mixed gases are obtained by dropping sulfuric acid into a red-hot retort of platinum or earthenware, the acid being decomposed as follows: $H_2SO_4 = H_2O + SO_2 + O.$

The gases are passed through condensers and over coke moistened with sulfuric acid, whereby the water is removed, and finally over platinized asbestus contained in glazed earthenware pipes.

Physical Properties.—Above 16° sulfuric oxid is a colorless mobile liquid which boils at 46.2° and has a specific gravity 1.94 at 16°. The liquid has a very high rate of expansion, the coefficient being 0.0027 for temperatures between 25° and 45°. At lower temperatures it is a solid which crystallizes in white silky needles and melts at 14.8°.

Chemical Properties.—Sulfuric oxid fumes strongly in the air and dissolves in water with a hissing sound to form H_2SO_4. Its attraction for water is so strong that it dehydrates organic matters, leaving them charred. It burns the skin and is an active poison. With metals it forms sulfids and oxids, and with oxids of metals it forms sulfates. At red heat it dissociates into SO_2 and O. It is a

nonconductor of electricity and is not decomposed by the electric spark.   It dissolves sulfur to form S_2O_6.

The formation of sulfuric oxid and its solution in water are both strongly exothermic, as is shown by the following equation:

$$(S,O_2) = 71,000 \text{ cal.}   (SO_2,O) = 32,200 \text{ cal.}   (S,O_3) = 103,200 \text{ cal.}$$
$$(SO_3, \text{ Aq.}) = 39,100 \text{ cal.}   (S,O_3, \text{ Aq.}) = 142,400 \text{ cal.}$$
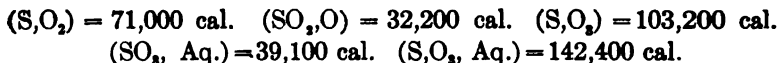
Sulfur burns to SO_2 instead of SO_3, furnishing an exception to the rule that that combination is formed by which the most heat is evolved.   This is explained on the supposition that the formation of SO_3 is very slow while that of SO_2 is rapid.   Finely divided platinum acts catalytically to accelerate the formation of SO_3.

SULFUR SESQUIOXID.

Formula S_2O_3.   Molecular weight 112.

Preparation.—Sulfur sesquioxid is best prepared by the union of sulfur and sulfuric oxid.   Well-dried flowers of sulfur are added by littles to freshly prepared sulfuric oxid in a test-tube immersed in cold water.   As the blue drops are formed, the tube is tilted so that they adhere to its sides. When enough has been formed, the excess of SO_3 is poured off and the residue evaporated away at a temperature not above 35°.   A blue solution of the sesquioxid is obtained by heating sulfur with disulfuric acid, $H_2S_2O_7$.

Properties.—Sulfur sesquioxid is a malachite green crystalline solid. It is unstable, decomposing slowly in the air and rapidly when heated, yielding SO_2 and S.   It acts vigorously with water, forming several acids of sulfur and free sulfur.   It dissolves in sulfuric and disulfuric acids, but not in sulfuric oxid.

PERSULFURIC OXID (SULFUR PEROXID, SULFUR HEPTOXID).

Formula S_2O_7.   Molecular weight 176.

Preparation.—Persulfuric oxid is formed by the silent electric discharge through a mixture of SO_2 or SO_3 with oxygen.   A solution is obtained by electrolizing dilute sulfuric acid (35 per cent H_2SO_4), or by adding aqueous hydrogen peroxid to strongly cooled sulfuric acid.

Properties.—Persulfuric oxid is an oily liquid which at 0° solidifies in transparent needle-shaped crystals.   It is unstable readily decomposing into sulfuric oxid and oxygen, and is a powerful oxidizer.   It dissolves in water, forming first persulfuric acid, HSO_4, which immediately dissociates into H_2SO_4 and oxygen.

ACIDS OF SULFUR.

Sulfur acts with all its valences to form three regular acids as follows:

Hyposulfurous acid (Ortho), $H_2S^{II}O_2$

$$\begin{array}{c} H-O \\ H-O \end{array}\!\!\Big\rangle S$$

Sulfurous acid (Monometa), $H_2S^{IV}O_3$

$$\begin{array}{c} H-O \\ H-O \end{array}\!\!\Big\rangle S = O$$

Sulfuric acid (Dimeta), $H_2S^{VI}O_4$

$$\begin{array}{c} H-O \\ H-O \end{array}\!\!\Big\rangle S\!\!\Big\langle\begin{array}{c} O \\ O \end{array}$$
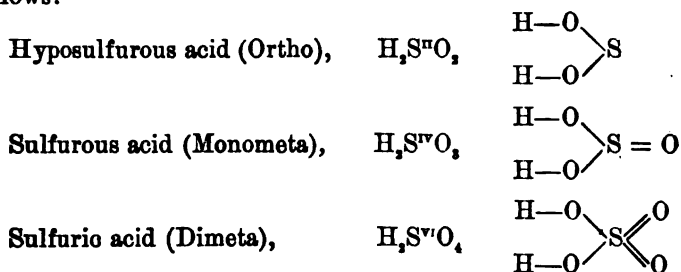
Two other acids are obtained by the union and condensation of two molecules of sulfuric acid, a molecule of water being taken away in the first case and a molecule of hydrogen in the second:

Sulfuric acid
(two molecules), $H_4S_2O_8$

$$\begin{array}{c} H-O \\ H-O \end{array}\!\!\Big\rangle S\!\!\Big\langle\begin{array}{c} O \\ O \end{array}$$
$$\begin{array}{c} H-O \\ H-O \end{array}\!\!\Big\rangle S\!\!\Big\langle\begin{array}{c} O \\ O \end{array}$$

Disulfuric acid
(H₂O removed), $H_2S_2O_7$

$$\begin{array}{c} H-O \\ O \end{array}\!\!\Big\rangle S\!\!\Big\langle\begin{array}{c} O \\ O \end{array}$$
$$\begin{array}{c} O \\ H-O \end{array}\!\!\Big\rangle S\!\!\Big\langle\begin{array}{c} O \\ O \end{array}$$

Persulfuric acid
(H₂ removed), $H_2S_2O_8$

$$\begin{array}{c} H-O \\ O \end{array}\!\!\Big\rangle S\!\!\Big\langle\begin{array}{c} O \\ O \end{array}$$
$$\begin{array}{c} O \\ H-O \end{array}\!\!\Big\rangle S\!\!\Big\langle\begin{array}{c} O \\ O \end{array}$$
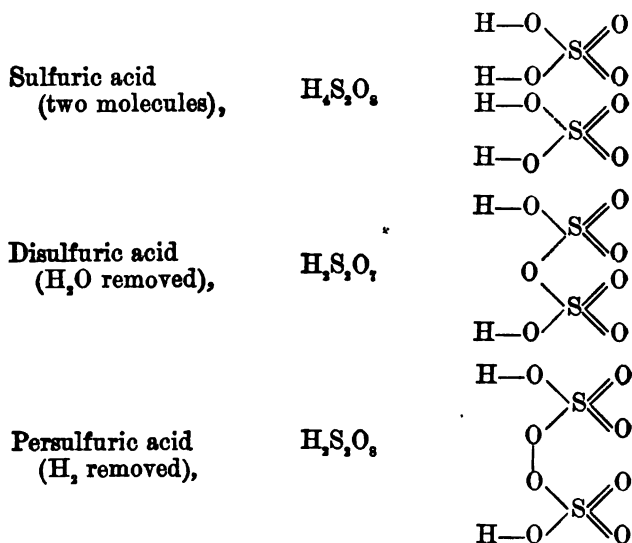
There is a mixed acid which may be supposed to be derived from sulfuric acid by replacing one of its linking atoms of oxygen by sulfur:

Thiosulfuric acid, $H_2S_2O_3$

$$\begin{array}{c} H-O \\ H-S \end{array}\!\!\Big\rangle S\!\!\Big\langle\begin{array}{c} O \\ O \end{array}$$
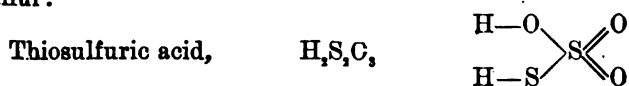
In another series of compounds, called thionic acids, each molecule contains two or more atoms of sulfur. While the structure cannot be stated with certainty, the following formulas are approximately correct:

Dithionic acid, $H_2S_2O_6$

$$H—O—SO_2$$
$$|$$
$$H—O—SO_2$$

Trithionic acid, $H_2S_3O_6$

$$H—O—SO_2 \diagdown$$
$$\qquad\qquad\qquad S$$
$$H—O—SO_2 \diagup$$

Tetrathionic acid, $H_2S_4O_6$

$$H—O—SO_2 \diagdown$$
$$\qquad\qquad\qquad S_2$$
$$H—O—SO_2 \diagup$$

Pentathionic acid, $H_2S_5O_6$

$$H—O—SO_2 \diagdown$$
$$\qquad\qquad\qquad S_3$$
$$H—O—SO_2 \diagup$$
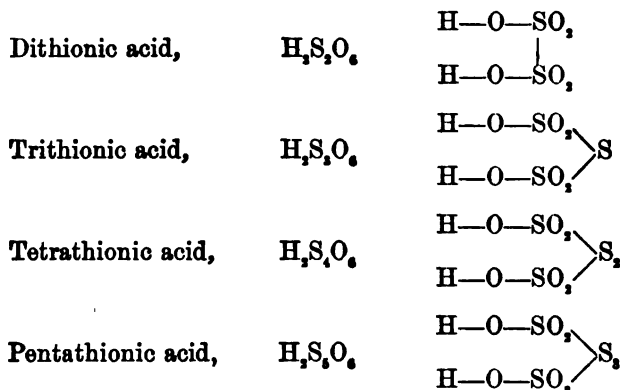
The acids of sulfur are all dibasic, with the possible exception of persulfuric acid, and form acid, normal and double salts. They are all liquids and mix with water in all proportions. They yield two sets of ions as one or both atoms of hydrogen may separate. From sulfuric acid, for example, we have:

$$H_2SO_4 = \overset{+}{H}' + \overset{+}{H}' + \overset{\bullet-}{SO}'_4, \quad \text{or} \quad H_2SO_4 = \overset{+}{H}' + H\overset{-}{S}O'_4.$$

HYPOSULFUROUS ACID.

Formula H_2SO_2.   Molecular weight 66.   Density (probably) 33.

Preparation.—Hyposulfurous acid is formed:

1. By the action of metals (Zn, Fe, Sn) upon sulfurous acid, the nascent hydrogen set free by the action of the metal upon a portion of the acid reducing another portion so that no hydrogen is evolved:

$$2H_2SO_3 + Zn = ZnSO_3 + H_2O + H_2SO_2.$$

2. By the action of sulfuric or oxalic acid upon sodium hyposulfite:

$$H_2SO_4 + Na_2SO_2 = Na_2SO_4 + H_2SO_2.$$
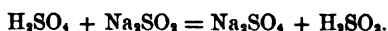
A solution is easily obtained by adding dilute oxalic acid to a solution of a hyposulfite ($NaHSO_2$).

Properties.—Hyposulfurous acid has not been obtained free from water and other impurities. The solution has an orange-yellow color, reduces and bleaches powerfully, and decomposes quickly, yielding first thiosulfuric acid and finally sulfurous oxid, sulfur and water: $2H_2SO_2 = 2H_2O + SO_2 + S.$

Hyposulfites.—The hyposulfites are somewhat more stable than the acid. Only a few of them have been prepared, such as the acid and normal sodium salts, $NaHSO_2$ and Na_2SO_2. These must not be confounded with the commercial hyposulfites, which are salts of thiosulfuric acid : $H_2S_2O_3$.

SULFUROUS ACID.

Formula H_2SO_3. Molecular weight 82. Density (probably) 41.

Preparation.—Sulfurous acid is formed by the union of sulfurous oxid with water: $SO_2 + H_2O = H_2SO_3$. It is therefore a product of any reaction by which SO_2 is formed in the presence of moisture.

Properties.—Sulfurous acid has not been obtained free from water. Its solution is colorless and acid, and has the odor of sulfurous oxid. When cooled to 0° the crystalline hydrate, H_2SO_3, $8H_2O$, separates. Other cryohydrates have been obtained with 6, 10, and 14 molecules of water respectively.

Sulfurous acid is unstable, readily giving off SO_2 when warmed, and losing the whole of the gas at 100°. On exposure to air it gradually absorbs oxygen and becomes H_2SO_4. It is decomposed by many reagents with the formation of polythionic acids. It is a reducing agent and possesses in general the properties of SO_2. Its total heat of formation is 147,624 calories. Its dissociation is small and the solution contains mainly the hydrosulfite ion HSO_3'.

Sulfites.—The alkaline sulfites are formed by passing SO_2 through solutions of alkaline hydroxids, and are easily soluble in water. When the oxid is in excess the acid salt is formed, and when the hydroxid is in excess the normal salt is obtained; $KHO + SO_2 = KHSO_3$, $2KHO + SO_2 = H_2O + K_2SO_3$. Most sulfites are decomposed by sulfuric acid with evolution of SO_2, which is recognized by its odor. They give with barium chlorid a white precipitate which is soluble in hydrochloric acid.

Disulfurous Acid, $H_2S_2O_5$, and **disulfites** have been prepared.

SULFURIC ACID.

Formula H_2SO_4. Molecular weight 98. Specific gravity 1.854 at 0°.

History. — Sulfuric acid seems to have been known to the Arabian philosopher Geber in the eighth century. Basil Valentine prepared it from ferrous sulfate or green vitriol in the fifteenth century, and it was called *oil of vitriol.* The manufacture of the acid began in England early in the eighteenth century by methods not very different from those now used. Its composition was determined by Lavoisier.

Occurrence. — Sulfuric acid occurs free in small quantities, certain rivers and springs in volcanic regions containing from 0.1 to 0.5 per cent of it. It is abundantly represented by native sulfates, the more important of which are the alums (sulfates of aluminum, with potassium and other metals), barytes (barium sulfate), gypsum (calcium sulfate), copperas (iron sulfate), Epsom salts (magnesium sulfate), celestite (strontium sulfate).

Preparation. — Sulfuric acid is formed by many chemical processes, among which the most important are:

1. By direct union of SO_3 with water or SO_2 with hydrogen peroxid :
$$SO_3 + H_2O = H_2SO_4. \quad SO_2 + H_2O_2 = H_2SO_4.$$

2. By heating ferrous sulfate in the presence of water :
$$FeSO_4 + H_2O = FeO + H_2SO_4.$$

3. By the oxidation of sulfur or sulfurous oxid in the presence of water:
$$SO_2 + O + H_2O = H_2SO_4.$$
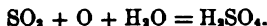
Manufacture of Sulfuric Acid. — For the commercial manufacture of sulfuric acid the third method is used. The sulfurous oxid is obtained by burning sulfur or iron pyrites (FeS_2), and is oxidized by nitric acid to sulfuric oxid, which in turn unites with water to form sulfuric acid. The chemical reactions are complicated and probably do not always take place in the same way. They may be represented, however, as follows:

1. Nitric acid is decomposed by sulfurous oxid with formation of sulfuric acid and liberation of nitrogen dioxid (or nitrogen trioxid):
$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2.$$

2. Nitrogen dioxid with water oxidizes the sulfurous oxid to sulfuric acid and is itself reduced to nitrogen monoxid :
$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO.$$

8. The oxygen of the air converts NO back into NO_2 or N_2O_3:

$$NO + O = NO_2 \quad \text{or} \quad 2NO + O = N_2O_3.$$

The process is continuous. The nitric acid acts as a carrier of the oxygen of the air and is not itself consumed. The water is introduced as steam.

If the supply of water is not sufficient a white solid crystalline compound is formed which may be regarded as either nitro-sulfonic acid, $\text{H—O} \diagdown \text{S} \diagup \text{O} $, or nitrosyl sulfuric acid, $\text{H—O} \diagdown \text{S} \diagup \text{O}$. On the addition of more water this is immediately decomposed into sulfuric acid and nitrogen trioxid:

$$2\,\begin{smallmatrix}H—O\\O_2N\end{smallmatrix}\!>\!S\!<\!\begin{smallmatrix}O\\O\end{smallmatrix} + H_2O = 2\,\begin{smallmatrix}H—O\\H—O\end{smallmatrix}\!>\!S\!<\!\begin{smallmatrix}O\\O\end{smallmatrix} + N_2O_3.$$
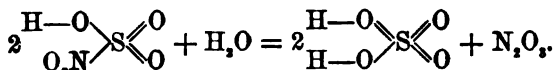
In practice the sulfuric-acid plant consists essentially of a furnace for burning the sulfur or pyrites, a series of leaden chambers, and two towers. After the gas leaves the furnace mixed with an abundance of air, it is conducted through what is called the *Glover tower*. This is filled with fragments of fire-brick, over which are made to flow the liquids from two vessels, one containing the nitroso sulfuric acid from the Gay-Lussac tower, and the other water or dilute sulfuric acid. By the dilution of the nitroso acid the oxids of nitrogen are set free and act upon the sulfurous oxid. At the same time the hot gas vaporizes the water and causes a concentration of the acid, which collects at the bottom of the tower. The residual gases pass on through the chambers, where they come in contact with steam and more nitrous fumes (generated by heating vessels which contain sodium nitrate and sulfuric acid), until they finally reach the *Gay-Lussac tower* at the end of the series, consisting mostly of atmospheric nitrogen and oxids of nitrogen. This tower is filled with coke, over which concentrated sulfuric acid is made to flow. This acid absorbs the nitrogen oxids and collects at the bottom of the tower as the saturated nitroso-sulfuric acid which is used in the Glover tower.

When the chamber acid has a specific gravity 1.5 (60%), it is drawn off (because above this it absorbs nitrous fumes) and concentrated in open leaden pans until the specific gravity is 1.73 (80%). A stronger acid attacks the lead, and so the evaporation is continued in platinum stills.

Sulfuric acid is also manufactured by what is called the *contact method*. Sulfurous oxid and air are passed over a heated catalyser such as finely divided platinum or ferric oxid. The oxygen of the air oxidizes the SO_2 to SO_3 and this is conducted into water to form H_2SO_4.

A comparatively pure acid is obtained from the commercial article by distilling it from platinum vessels. An aqueous solution first distils over and the temperature rises. At 330°, when about one third has passed over, the distillate has a specific gravity 1.84 at 15°, and contains only 2 per cent of water. This distillation does not remove arsenous oxid, as it is volatile and much of the so-called pure acid of commerce contains arsenic.

Illustrations.—Add a few cc. of H_2O_2 solution to a cylinder of SO_2. That sulfuric acid is formed may be shown by precipitating with barium chlorid.

The reduction of nitric acid may be shown by dropping into a jar of sulfurous oxid a stick or glass rod which has been dipped in strong nitric acid. Red fumes of NO_2 or N_2O_3 fill the jar at once, but soon disappear, being reduced by the SO_2 to NO, which is colorless. In a few minutes the wall of the jar becomes covered with white crystalline nitrosyl sulfuric acid. On adding water the crystals dissolve with effervescence and the red fumes reappear. The water in the vessel will be found to contain sulfuric acid.

Physical Properties.—Sulfuric acid is a colorless oily liquid nearly twice as heavy as water. If the concentrated acid be strongly cooled, crystals of anhydrous, H_2SO_4, are formed and may be separated from the liquid by a centrifugal machine. This solid melts at 10.5°, yielding a colorless liquid which has a specific gravity 1.854 at 0° and 1.837 at 15°, being a little lighter than the acid, which contains 2 per cent of water, whose specific gravity is 1.842 at 15°. The anhydrous acid may be cooled below zero without solidifying, but if it be shaken, or if a crystal of the acid be added, it becomes solid at once. The presence of even a small quantity of water lowers the freezing- and melting-point to zero.

Sulfuric acid does not boil at a constant temperature. When heated it fumes at 40°, and begins to boil with decomposition at 290°. As the boiling continues the temperature rises to 338°, at which point there is complete dissociation into SO_3 and H_2O. At this temperature the residue contains 1.5 per cent of water, and is the strongest acid which can be obtained by distillation. The acid of this strength is obtained by boiling either the dilute acid or the acid containing SO_3 in solution. Because of its decomposition the density of the acid cannot be experimentally determined. Its reactions, however, its derivatives, and its specific heat point to the formula H_2SO_4 and the density 49.

Sulfuric acid is a conductor of electricity and an electrolyte. Its specific heat is 0.355 and its molecular heat 34.79. The specific gravity of the aqueous acid varies between such large limits that it affords a convenient means of determining the percentage of acid in any solution. The specific gravity is taken with a hydrometer and the strength of the acid read from a table prepared for the purpose.

Chemical Properties.—Sulfuric acid is unstable, easily reduced, and chemically very active. It dissolves all the metals except gold, platinum, iridium, and rhodium. It is able to expel most of the acids from their salts, and hence is used in their manufacture; for example: $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$. It dissociates at red heat as follows: $H_2SO_4 = SO_2 + H_2O + O$, and may thus be used as a source of oxygen, the SO_2 being separated and reconverted into sulfuric acid to be used again. It is also reduced, yielding the dioxid when heated with carbon, phosphorus, sulfur, and some metals (Hg, Cu). It chars organic matters by extracting water from them.

Sulfuric acid has a strong attraction for water. It takes moisture from the air, diluting and increasing in volume. It is a powerful desiccating agent, and is used in drying air and other gases. It mixes with water in all proportions evolving much heat and diminishing in volume. The greatest heat and the greatest lessening of volume occur when the acid and water are mixed in the proportion of H_2SO_4 to $2H_2O$. The contraction is about eight per cent, and the temperature rises above 100°. This is the ortho acid H_6SO_6 which has a specific gravity 1.655. It may also be formed by evaporating the dilute solution at 100°. The monometa acid H_4SO_5 is obtained by cooling to zero a mixture of the acid and water in the proportion H_2SO_4 to H_2O. It separates in prismatic crystals of specific gravity 1.78 and boiling-point 7.5.

Sulfuric acid yields two colorless, negative, active ions, the bivalent sulfate ion SO_4'' and the univalent hydrosulfate ion HSO_4'. The strong acid contains mainly the latter, but as the acid is diluted this ion dissociates into $H\cdot$ and SO_4''. The degree of dissociation is about as follows: In the twentieth normal acid 62 per cent, in the two hundredth normal 85 per cent, in the three hundredth normal 89 per cent, in the one thousandth normal 97 per cent. The dissociation is complete only when a mol of the acid is contained in about 2000 liters of water. The strength of sulfuric acid is about half that of hydrochloric acid.

The heat of formation of sulfuric acid is shown by the following equations:

Heat of formation from H_2O and SO_3, (H_2O, SO_3) = 21,320 cal.
Heat of formation from the elements, (H_2, S, O_4) = 192,920 cal.
Heat of solution, $(H_2SO_4, Aq.)$ = 17,800 cal.
Total heat of formation and solution, $(H_2, S, O_4, Aq.) = 210,720$ cal.

Illustrations.—To show the action of sulfuric acid :

a. Dip a splinter of wood into the strong acid: it is charred at once.

b. Write with the dilute acid upon paper with a brush or the finger and warm over the lamp. As the water evaporates the acid concentrates and presently the letters appear by the blackening of the paper.

c. Place in a beaker a gram of sugar and just enough water to dissolve it and add a cc. of strong sulfuric acid.

To show the contraction of a mixture of the acid and water fill a long tube three fifths full of the acid and add water to nearly fill the tube. Mark the surface, then mix the liquids, and note that the surface is below the mark.

To show the heat of mixture fill a beaker one third full of water and pour in the acid slowly, stirring with a test-tube containing ether. The ether soon boils and may be lighted at the mouth of the tube.

Its action upon metals is shown by adding zinc to the dilute acid, or by heating copper with the strong acid. The first yields hydrogen, the second sulfurous oxid.

Its action upon salts is shown by adding the strong acid to sodium chlorid. There is a rapid evolution of hydrogen chlorid.

Physiological Properties.—Sulfuric acid is an active corrosive poison. It burns the skin and chars the flesh, making distressing sores. When it comes in contact with the body or the clothes it should be neutralized at once with ammonia.

Tests.—Sulfuric acid is recognized by its weight, by its carbonizing action upon organic bodies, and by its forming a white insoluble precipitate with barium chlorid, $H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl$.

Uses.—Hardly any other substance, except water, finds so many applications in the arts as sulfuric acid. It is used in the manufacture of nitric, hydrochloric, phosphoric, citric, and tartaric acids; of soda, phosphorus, alum, glucose, alkalies, fertilizers, nitroglycerine, and dynamite; in dyeing, bleaching, and calico-printing; in refining petroleum and recovering ammonia from gas liquors. In the laboratory its uses are manifold. It is one of the most convenient and effective of drying agents, especially for gases.

Sulfates.—Sulfuric acid is dibasic and gives acid, normal and double salts. Besides these there are salts of the ortho and monometa acids, examples of which have already been given. Sulfates are formed by the action of sulfuric acid upon metals and their oxids, hydroxids, and salts. They are generally crystalline solids and are mostly soluble in water. Barium sulfate is insoluble in water and the sulfates of lead, calcium, and strontium are sparingly soluble.

DISULFURIC ACID (PYROSULFURIO ACID, FUMING SULFURIC ACID).

Formula $H_2S_2O_7$. Molecular weight 178. Specific gravity 1.88.

History.—Fuming sulfuric acid was originally manufactured at Nordhausen in the Hartz, and hence was called Nordhausen sulfuric acid. It was made by heating ferrous sulfate or green vitriol. At the present day Bohemia furnishes the greater part of the commercial acid.

Preparation.—Fuming sulfuric acid is a solution in varying proportions of sulfuric oxid in sulfuric acid. It is therefore formed whenever sulfuric acid is made with an excess of sulfuric oxid. It may be prepared—

1. By dissolving sulfuric oxid in sulfuric acid:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

2. By heating sulfates and pyrosulfates in the presence of a limited quantity of water. When ferrous sulfate is heated with free access of air it first loses its water of crystallization, then oxidizes to ferric sulfate, $Fe_2(SO_4)_3$, or the basic ferric sulfate, $Fe_2S_2O_9$, and these at a higher temperature decompose into ferric trioxid and sulfuric oxid:

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.   Fe_2S_2O_9 = Fe_2O_3 + 2SO_3.$$

The SO_3 is conducted into sulfuric acid or into water until the SO_3 is in excess. The residue of Fe_2O_3 is the *colcothar* of commerce, used as a paint and a polishing material.

The sulfuric oxid may also be obtained from sodium disulfate (formed by heating acid sodium sulfate) by the action of heat or sulfuric acid:

$$2HNaSO_4 = H_2O + Na_2S_2O_7.   Na_2S_2O_7 + H_2SO_4 = 2HNaSO_4 + SO_3.$$

Physical Properties.—Fuming sulfuric acid is a colorless oily liquid of specific gravity 1.86 to 1.89. The acid has usually a brown color due to suspended carbon from organic matters accidentally introduced. It fumes strongly in the air, the escaping SO_3 uniting with moisture to form H_2SO_4, and dissolves in water in all proportions. When the strong solution is cooled colorless crystals of

H_2SO_4,SO_3 or $H_2S_2O_7$ separate. This is the *disulfuric acid* proper. It melts at 35°. The solid acid is now an article of commerce.

Chemical Properties.—Disulfuric acid, being a loose compound of sulfuric acid and sulfuric oxid, is unstable and chemically active. It decomposes slowly in the air and rapidly when heated. Its attraction for water is even greater than that of sulfuric acid and it unites with it with a hissing sound. Its general properties are those of its constituents.

Uses.—Fuming sulfuric acid is used for dissolving indigo and in the manufacture of various anilin dyes, particularly artificial alizarine.

Disulfates.—From disulfuric acid are derived salts which are quite stable. They are usually obtained by heating the sulfates. At higher temperatures they decompose, yielding sulfates again and sulfuric oxid.

PERSULFURIC ACID.

Formula HSO_4 or $H_2S_2O_8$. Molecular weight 97 or 194.

Preparation and Properties.—Persulfuric acid is formed by the solution of persulfuric oxid in water : $S_2O_7 + H_2O = 2HSO_4$; but the compound decomposes at once with the liberation of oxygen:

$$2HSO_4 + H_2O = 2H_2SO_4 + O.$$
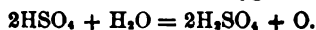
It is more stable in sulfuric-acid solution and is formed at the anode when the acid is electrolized in a divided cell. The acid itself has not been isolated. It is very unstable and a powerful oxidizing agent.

Persulfates.—The persulfates are more stable than the acid, but are vigorous oxidizing and bleaching agents. The potassium salt is obtained as a crystalline solid by the action of nascent oxygen in the electrolysis of hydrogen-potassium sulfate in a divided cell: $2HKSO_4 + O = H_2O + KSO_4$. Ammonium persulfate, NH_4SO_4, and barium persulfate, $Ba(SO_4)_2$, have been prepared.* The latter is quite soluble in water and therefore barium chlorid gives no precipitate with persulfates, a fact which serves to distinguish them from sulfates. If, however, the mixture be warmed, the persulfate decomposes, the precipitate appears, and chlorin is evolved.

THIOSULFURIC ACID (HYPOSULFUROUS ACID).

Formula $H_2S_2O_3$. Molecular weight 114.

Preparation and Properties.—When a weak acid acts upon a dilute solution of sodium thiosulfate, thiosulfuric acid is supposed to be separated as follows:

$$2HCl + Na_2S_2O_3 = 2NaCl + H_2S_2O_3.$$
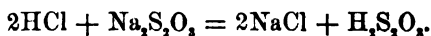
The acid cannot be isolated, because it decomposes at once into sulfurous oxid, water, and sulfur.

Thiosulfates.—Thiosulfates are numerous and quite stable. They are formed when sulfur is digested with sulfites or hydroxids,

$$Na_2SO_3 + S = Na_2S_2O_3,$$
$$6NaHO + 4S = 2Na_2S + 3H_2O + Na_2S_2O_3,$$
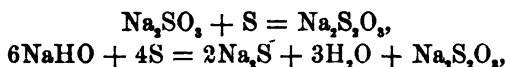
and when sulfurous oxid acts upon sulfids.   In the latter case sulfur and a sulfite are first separated,

$$3SO_2 + 2Na_2S = 2Na_2SO_3 + 3S,$$
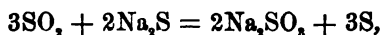
and these react to form the thiosulfate.

The thiosulfates are decomposed by acids with liberation of sulfur and sulfurous oxid.   The most important of these salts is the sodium thiosulfate which is much used in photography under the name of *hyposulfite of soda* or simply *hypo.*

THIONIC ACIDS.

Dithionic Acid, $H_2S_2O_6$.—Dithionic acid is prepared by the action of dilute sulfuric acid upon barium dithionate :

$$BaS_2O_6 + H_2SO_4 = BaSO_4 + H_2S_2O_6.$$
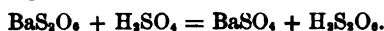
The solution may be concentrated in vacuo until it has a specific gravity 1.847.   On further concentration it decomposes into sulfuric oxid and sulfuric acid, $H_2S_2O_6 = SO_3 + H_2SO_4$. The free acid has not been obtained.

Dithionates are well-defined crystalline salts which decompose when heated into sulfates and sulfurous oxid.

Trithionic Acid, $H_2S_3O_6$.—A dilute solution is obtained by treating the potassium salt with hydrofluosilicic acid or perchloric acid:

$$H_2SiF_6 + K_2S_3O_6 = K_2SiF_6 + H_2S_3O_6.$$
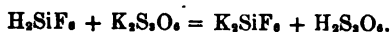
The solution is colorless and odorless and has a bitter, acid taste.   When heated it decomposes, yielding sulfuric acid, sulfurous oxid, and sulfur.

Trithionates are more stable than the acid, but undergo a similar decomposition when heated.

Tetrathionic Acid, $H_2S_4O_6$.—This acid is known only in dilute aqueous solution which may be boiled, but on concentration decomposes into sulfuric acid, sulfurous oxid, and sulfur. The solution is obtained by treating the barium salt with sulfuric acid : $BaS_4O_6 + H_2SO_4 = BaSO_4 + H_2S_4O_6.$

Tetrathionates are all soluble in water, from which they cannot be easily separated without decomposition. With sodium amalgam or potassium sulfid they yield thiosulfates and sulfur : $K_2S_4O_6 + K_2S = 2K_2S_2O_3 + S.$

When hydrogen sulfid is passed for a long time through strong sulfurous acid, the solution will be found to contain all the thionic acids, to-

gether with sulfuric and probably thiosulfuric acids. This liquid is known as *Wackenroder's solution.* If the passage of the hydrogen sulfid be continued until action ceases, it will be found that the thionic acids have decomposed and that nothing remains except sulfur and water. The final result of the action is, therefore, represented by the equation :

$$H_2SO_3 + 2H_2S = 3H_2O + 3S.$$
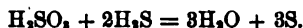
OXYCHLORIDS OF SULFUR.

Several oxychlorids of sulfur are known. They are best understood by supposing them to be derived from the acids of sulfur by the replacement of hydroxyl with chlorin. The following table shows the names and formulas of those best known and their relation to the acids:

Sulfurous oxychlorid, $Cl\diagdown SO$; (Thionyl chlorid), $Cl\diagup$.

Sulfuric hydroxychlorid, $Cl\diagdown SO_2$ (Chlorsulfonic acid), $H—O\diagup$

Sulfuric oxychlorid, $Cl\diagdown SO_2$; (Sulfuryl chlorid), $Cl\diagup$

Disulfuric oxychlorid, $Cl—SO_2\diagdown O$ (Disulfuryl chlorid), $Cl—SO_2\diagup$

Sulfurous Oxychlorid (Thionyl chlorid), $SOCl_2$, is obtained by the action of phosphorus pentachlorid upon sulfurous oxid or sulfites :

$$SO_2 + PCl_5 = POCl_3 + SOCl_2;$$
$$Na_2SO_3 + 2PCl_5 = 2NaCl + 2POCl_3 + SOCl_2.$$
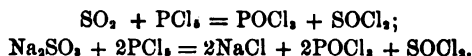
Sulfurous oxychlorid is a colorless, highly refractive, fuming liquid which boils at 78°. It has a penetrating odor and its vapor attacks the eyes and respiratory organs. It is decomposed by water, hydrogen sulfid, and many other reagents.

Sulfuric Hydroxychlorid (Chlorsulfonic acid), $SO_2Cl(HO)$, is formed—

1. By the action of phosphorus oxychlorid upon sulfuric acid:

$$2H_2SO_4 + POCl_3 = HCl + HPO_3 + 2SO_2Cl(HO).$$
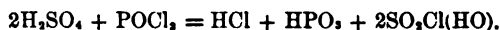
2. By direct union of sulfuric oxid and hydrochloric acid :

$$SO_3 + HCl = SO_2Cl(HO).$$
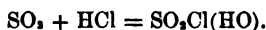
3. By the action of hydrochloric acid upon solid disulfuric acid:

$$2HCl + H_2S_2O_7 = H_2O + 2SO_2Cl(HO).$$
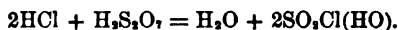
This compound is a colorless, fuming liquid which has a specific gravity 1.78, boils at 155°, and has a penetrating odor. Dissociation begins at the boiling temperature and is complete at 440°. It decomposes violently in contact with water into hydrochloric and sulfuric acids.

Sulfuric Oxychlorid (Sulfuryl chlorid), SO_2Cl_2, was first prepared by Regnault in 1838 by the continued action of sunlight upon a mixture of

equal volumes of chlorin and sulfurous oxid. This mixture is also caused to unite by the presence of a little camphor. It is further obtained by heating chlorsulfonic acid in a closed tube to 180° for 12 hours:

$$2SO_2Cl(HO) = SO_2Cl_2 + H_2SO_4.$$
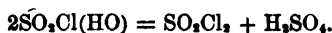
Sulfuric oxychlorid is a colorless, suffocating, fuming liquid which boils at 70° and has a specific gravity 1.71 at 0°. It decomposes energetically in the presence of water, first yielding chlorsulfonic acid and finally sulfuric and hydrochloric acids. Its density is normal at 184°. Above this it decomposes, and at 440° the dissociation into SO_2 and Cl_2 is complete.

Disulfuric Oxychlorid (Disulfuryl chlorid), $S_2O_5Cl_2$, is formed by the action of SO_2 upon PCl_5, S_2Cl_2, SO_2Cl_2, or NaCl; also by the action of PCl_5 upon $SO_2Cl(HO)$. It is a heavy, oily, highly refractive, fuming liquid which boils at 153° and has a specific gravity 1.819 at 0°. Its density is normal at the boiling-point. Above this dissociation begins and is complete at 240°. It dissolves in water with hissing and with gradual decomposition, giving first chlorsulfonic acid and finally sulfuric and hydrochloric acids.

OXYBROMIDS OF SULFUR.

Two oxybromids of sulfur are said to have been prepared:

Sulfurous Oxybromid, $SOBr_2$, by the action of sodium bromid upon sulfurous oxychlorid: $2NaBr + SOCl_2 = 2NaCl + SOBr_2$; and

Sulfuric Oxybromid, SO_2Br_2, by the action of bromin upon sulfurous oxid in sunlight: $SO_2 + Br_2 = SO_2Br_2$. The former is a crimson liquid and the latter a white crystalline solid.

No oxyiodids and oxyfluorids of sulfur have been prepared.

SELENIUM.

Symbol Se.   Atomic weight 79.   Molecular weight 158.   Density 79·
Valence II, IV, VI.   Specific gravity 4.3 to 4.8.   Melting-point 217°.

Occurrence.—Selenium is widely distributed in small quantities. It rarely occurs free. Its more common combinations are with lead, copper, bismuth, mercury, silver, and sulfur as selenids and double selenids. It is often associated with native sulfids and native sulfur.

History.—Selenium was discovered by Berzelius in 1817. He obtained it from the deposit in the leaden chambers of a sulfuric-acid manufactory in Gripsholm in Sweden. He called it *selenium,* from the Greek word which means *moon,* because of its resemblance to the element tellurium (*tellus,* the earth), discovered a short time before.

Preparation.—Selenium is obtained—

1. By reducing selenous acid with sulfurous oxid :

$$H_2SeO_3 + 2SO_2 + H_2O = 2H_2SO_4 + Se.$$
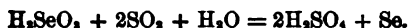
2. By the action of hydrochloric acid upon potassium selenocyanid:

$$KCNSe + HCl = KCl + HCN + Se.$$
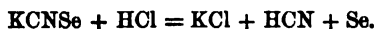
3. By exposing a solution of an alkali selenid to the action of the air:

$$K_2Se + O = K_2O + Se.$$
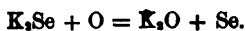
The usual source of selenium is the residues of the sulfuric-acid manufactory. When the selenium-bearing pyrites is burned, the volatilized selenium and selenous oxid are deposited in the flues, in the Glover tower, and in the chambers. From this deposit the selenium may be obtained in the following ways:

1. The residue is boiled with dilute sulfuric acid with addition of nitric acid or potassium chlorate, whereby selenic acid is formed. This boiled with strong hydrochloric acid is reduced to selenous acid, which is further reduced to selenium by a stream of sulfurous oxid.

2. The residue is digested with potassium cyanid, whereby potassium selenocyanid is formed, and this is reduced by hydrochloric acid.

3. The deposit is fused with sodium nitrate and sodium carbonate and extracted with water. The solution, which contains alkali selenid, slowly deposits the selenium on exposure to the air.

Physical Properties.—Selenium is an amorphous or crystalline solid which melts at 217° and boils at 650°. The vapor is dark yellow and when suddenly cooled condenses to a fine red powder called *flowers of selenium.* It may be sublimed and distilled *in vacuo* or in an indifferent gas. When heated in hydrogen the sublimate is black. The vapor density diminishes as the temperature rises until at 1420° it is 82, which is but little above the normal, 79, and indicates the molecular formula Se_2.

Selenium presents three physical forms which are probably distinct allotropic modifications, as follows:

1. *Liquid or vitreous selenium.*—This form is liquid above 220° and below this temperature becomes more and more viscid until at 30° it is quite hard and brittle with a vitreous fracture. On pulverizing it yields a red amorphous powder which seems to be identical with the powder obtained by reducing selenous acid. Liquid selenium, both vitreous and amorphous, is slightly soluble in carbon disulfid and has a specific gravity 4.3 to 4.5.

2. *Red crystalline selenium.*—This is a red powder composed of. monoclinic crystals, and is obtained from solution of selenium in carbon disulfid. It is isomorphous with monoclinic sulfur and has specific gravity 4.5.

8. *Metallic selenium.*— This is a gray or black crystalline solid of specific gravity 4.5 to 4.8.   It has a metallic appearance and conducts electricity. Its electric conductivity is peculiarly affected by light, being twice as great in diffused daylight as it is in the dark.

Chemical Properties.—In all its chemical properties selenium closely resembles sulfur.   It is somewhat less negative than sulfur, has valences II, IV, and VI, is insoluble in water, and is chemically inactive until it is heated.   It burns in the air with a reddish flame to SeO_2, which has a disagreeable odor resembling that of decaying horse-radish.   With water and ozone it forms selenic acid.   It dissolves in sulfuric and hot nitric acids, yielding selenous and selenic acids.   It unites readily to hydrogen, phosphorus, the halogens, and the metals to form selenids.

SELENIUM COMPOUNDS.

Selenium forms numerous compounds exactly corresponding to those of sulfur.

SELENIUM AND HYDROGEN.

Hydrogen Selenid. H_2Se, is formed by direct union when selenium is heated in hydrogen; also by the action of dilute acids (HCl and H_2SO_4) upon selenids (of K and Fe):

$$FeSe + H_2SO_4 = FeSO_4 + H_2Se.$$

It is a colorless gas with a very disagreeable and irritating odor. It is quite poisonous, destroying for a time the sense of smell and producing headache.   It is more soluble than H_2S, and the solution reddens litmus.   It is decomposed by heat and the electric spark, and precipitates metals from solution as selenids.   It burns with a blue flame to SeO_2 and H_2O.   Its formation is endothermic, the equation being $(H_2Se) = -11,100$ cal.

No compound of selenium corresponding to H_2S_2 is known.

Selenids.—The selenids may be regarded as simple binary compounds, or as derivatives of hydrogen selenid.   The alkali selenids are soluble, the others mostly insoluble, in water.

SELENIUM HALIDS.

Selenium Fluorid, Se_2F_2, soluble in hydrochloric acid and decomposable by water, is said to be formed as a crystalline solid when selenium vapor is passed over lead fluorid.

Selenium Dichlorid, Se_2Cl_2, is obtained by the direct union of selenium and chlorin, or by passing HCl through a strong acid solution of selenium. It is a reddish, brown, oily liquid with a disagreeable selenous odor. Its specific gravity is 2.9 and its heat of formation 22,150 cal.

Selenium Tetrachlorid, $SeCl_4$, is formed by the action of chlorin upon selenium or selenium dichlorid, or by heating selenium oxid with phosphorus pentachlorid. It is a yellowish-white crystalline solid which sublimes without melting. It dissociates at 200° and dissolves in water with decomposition. Heat of formation, 46,160 cal.

Selenium Dibromid, Se_2Br_2, is formed by direct union of selenium and bromin. It is a very dark-red liquid with unpleasant odor; specific gravity 3.6. It is decomposed by heat and in contact with water.

Selenium Tetrabromid, $SeBr_4$, is formed by the action of bromin upon selenium or selenium dibromid. It is best obtained by adding bromin to a solution of Se_2Br_2 in CS_2. It is a yellow crystalline solid which sublimes at 80°, partially decomposing, and condenses in black, shining, six-sided scales. It has a disagreeable odor and is decomposed by water.

Selenium Tribromchlorid, $SeBr_2Cl$, and **Selenium Bromtrichlorid,** $SeBrCl_3$, have been prepared. Both are colorless crystalline solids.

Selenium Diiodid, Se_2I_2, is formed by heating the elements together. It is a steel-gray crystalline metal-like solid which melts at 70° and is decomposed at a higher temperature or in contact with water.

Selenium Tetraiodid, SeI_4, is formed by heating together selenium and iodin, with the latter in excess, or by adding HI to H_2SeO_3. It is a dark-gray solid which melts at 80° to a very dark liquid.

OXIDS AND ACIDS OF SELENIUM.

Selenous Oxid, SeO_2, is prepared by burning selenium in a stream of oxygen. The oxid condenses in long white prisms which sublime at 300° without melting. It has a powerful odor and dissolves in water to form selenous acid.

Selenic Oxid, SeO_3, has not been isolated, but is represented in selenic acid and the selenates.

Selenous Acid, H_2SeO_3, is prepared by dissolving selenous oxid in hot water, or by heating selenium with nitric acid. It forms long colorless prisms which have a strong acid taste and decom-

pose when heated into SeO_2 and H_2O. Specific gravity 3; heat of formation $(Se,O_2,Aq.) = 57{,}200$ cal.

Selenites.—Selenous acid is dibasic and forms acid, normal and double salts. It also forms acid selenites united with the acid thus: $KHSeO_3, H_2SeO_3$. The alkali selenites are soluble, the others usually insoluble. They emit a horse-radish odor when heated on charcoal and precipitate red selenium when SO_2 is passed through their solution.

Selenic Acid, H_2SeO_4, is prepared (1) by the action of H_2S upon selenates, $H_2S + PbSeO_4 = H_2SeO_4 + PbS$; (2) by oxidizing selenous acid or selenites, as by adding bromin to silver selenite suspended in water, $Ag_2SeO_3 + Br_2 + H_2O = 2AgBr + H_2SeO_4$. The solution may be evaporated in the air until it has a specific gravity 2.6 and contains 94 per cent of the acid. It may be further concentrated *in vacuo* until the gravity is 2.627 and the acid content 97.4 per cent. It is a strongly acid, oily liquid resembling sulfuric acid. It mixes freely with water, dissolves metals, and is decomposed by heat. With HCl it evolves chlorin.

Selenates.—The metals generally form selenates which closely resemble the sulfates.

OXYCHLORID AND OXYBROMID OF SELENIUM.

Selenium Oxychlorid, $SeOCl_2$, is a fuming yellow liquid which solidifies at 10°, boils at 180°, and is decomposed by water. It is formed by the direct union of SeO_2 and $SeCl_4$.

Selenium Oxybromid, $SeOBr_2$, is a crystalline solid formed by melting together SeO_2 and $SeBr_4$.

SELENIUM AND SULFUR.

Selenium and sulfur melt together in all proportions seemingly without forming definite compounds. When hydrogen sulfid is passed through a solution of selenous acid, yellow selenous sulfid, SeS_2, is said to be precipitated; and when hydrogen selenid is passed into sulfurous acid a yellow precipitate falls which is supposed to be sulfurous selenid, SSe_2. When their joint solution in CS_2 is allowed to evaporate an isomorphous mixture of the two elements is obtained.

TELLURIUM.

Symbol Te. Atomic weight 128. Density 128. Molecular weight 256. Valence II, IV, VI. Specific gravity 6.24. Melting-point 452°.

Occurrence.—Tellurium occurs free in small quantities in Virginia, California, Hungary, Transylvania, Brazil, and Bolivia. It generally accompanies gold and silver. It is more usually found in the same countries as tellurids and double tellurids of gold, silver, lead, antimony, bismuth, and sulfur. It also occurs as the mineral tellurite, TeO_2.

History.—Tellurium was first prepared in 1798 by Klaproth, who named it after the Latin *tellus*, which means the *earth*. It was more fully investigated by Berzelius in 1832.

Preparation.—Amorphous tellurium is precipitated by sulfurous acid from solutions of tellurous acid, or by zinc from sulfuric-acid solutions of tellurium compounds. It is prepared from the native bismuth tellurid, Bi_2Te_3, as follows: The powdered ore is mixed with an equal weight of carbonate of sodium or potassium, made into thick paste with oil and heated to a white heat in a closed crucible. The mass is extracted with water and the filtered solution of alkali tellurid and sulfid is exposed to the air, when tellurium gradually separates as a gray powder. It is purified by distillation in a current of hydrogen. Cooled from fusion or obtained by sublimation it is crystalline.

Physical Properties.—Tellurium is a bluish-white, silver-like crystalline solid which melts at 452° and boils about 1380°. It gives a yellow vapor whose absorption spectrum consists of many fine lines extending from the yellow to the violet. It conducts electricity rather poorly and the conductivity is slightly increased in the light. It crystallizes in rhombohedra or in hexagonal prisms with rhombohedral summits. The specific gravity is 6.26.

Chemical Properties.—Physically tellurium resembles the metals, but chemically it is a non-metal, acting as a positive in only a few compounds. It is insoluble in water, but dissolves in cold fuming sulfuric acid, in hot solutions of alkali hydroxids, and in concentrated nitric acid. It is oxidized by nitric acid to H_2TeO_4.

TELLURIUM COMPOUNDS.

Tellurium is closely related to selenium and sulfur and forms compounds which are exactly analogous to those of these two elements.

TELLURIUM AND HYDROGEN.

Hydrogen Tellurid, H_2Te, is formed by the direct union of the elements when tellurium is heated in a current of hydrogen. It

is also obtained by the action of hydrochloric acid upon zinc tellurid, $ZnTe + 2HCl = ZnCl_2 + H_2Te.$

It is a colorless gas, not so poisonous as hydrogen selenid, and with an odor less offensive. It is unstable, is decomposed by heat, and the aqueous solution absorbs oxygen and deposits tellurium.

Tellurids.—Tellurium unites to most of the metals to form tellurids and double tellurids. The alkali compounds are soluble, while the others are mostly insoluble, in water.

TELLURIUM HALIDS.

Tellurium Tetrafluorid, TeF_4, is a colorless, transparent, deliquescent solid obtained by mixing tellurium oxid or acid with hydrofluoric acid.

Tellurium Dichlorid, $TeCl_2$, is formed by direct union of chlorin with tellurium in excess. It is a black amorphous solid which melts at 175° and boils at 327°, giving a red vapor.

Tellurium Tetrachlorid, $TeCl_4$, is obtained by heating tellurium with chlorin in excess. It is a colorless crystalline solid which melts at 214° and boils at 380°.

Tellurium Dibromid, $TeBr_2$, is obtained by union of bromin with tellurium in excess, or by fusing tellurium tetrabromid with excess of tellurium. It is a blackish-green, deliquescent, crystalline solid which melts at 305° and boils at 343°.

Tellurium Tetrabromid, $TeBr_4$, is a crystalline solid, red when hot and yellow when cold. It melts at 380° and boils at 414°. It is prepared by heating tellurium with bromin in excess in a current of carbon dioxid.

Tellurium Diiodid, TeI_2, is a black crystalline solid obtained by heating together tellurium and iodin in the proper proportions.

Tellurium Tetraiodid, TeI_4, is an iron-gray crystalline solid obtained by heating together in a closed flask tellurous and hydriodic acids.

OXIDS AND ACIDS OF TELLURIUM.

Tellurous Oxid (Tellurium dioxid), TeO_2.—Tellurium oxid occurs in nature as *tellurite* or *tellurium ocher*. It is prepared by burning tellurium or by oxidizing it with nitric acid. It is a white crystalline solid which melts at a red heat to a yellow liquid. The specific gravity varies from 5.65 to 5.90, according to the method of its preparation. It is almost insoluble in water, slightly soluble in acids, easily soluble in alkali hydroxids.

Telluric Oxid (Tellurium trioxid), TeO_3, is an orange-yellow crystalline solid obtained by heating telluric acid. It is nearly insoluble in water and cold acids, but dissolves in boiling acids and alkalies.

Tellurous Acid, H_2TeO_3, is obtained by dissolving tellurium in nitric acid and pouring the solution into water. The precipitate is dried over sulfuric acid. It is a white, amorphous solid with a metallic, bitter taste.

Tellurites.—Normal, acid, and double tellurites are formed; also molecular compounds with one or more molecules of the oxid or acid. Examples of the last are:

Potassium tetratellurite, $K_2TeO_3,3TeO_2$.

Superacid potassium tellurite, $HKTeO_3,H_2TeO_3$.

Telluric Acid, H_2TeO_4, is obtained by decomposition of barium tellurate, $BaTeO_4$, with sulfuric acid. On filtration and evaporation, crystals separate having the composition $H_2TeO_4,2H_2O$. When these crystals are heated to 160° the water is driven off and the acid is left as a white powder. At a higher temperature it separates into H_2O and TeO_3, and the latter finally into TeO_2 and O.

Tellurates.—The alkali tellurates are soluble in water, the others usually insoluble. Not only are acid, normal, and double tellurates formed, but also superacid tellurates of complex composition.

CHAPTER XXV.

GROUP VI A. THE CHROMOIDS. CHROMIUM GROUP.

Chromium 52.   Molybdenum 96.   Tungsten 184.   Uranium 239.

GENERAL PROPERTIES OF THE SUB-GROUP.

OF the elements of this sub-group chromium is the most important and the only one which is at all abundant.   Only a few molybdenum compounds are of commercial interest, while tungsten and uranium are rare elements scarcely seen, free or in their compounds, outside of chemical laboratories.

By reference to the periodic table it will be seen that each group of elements divides into two sub-groups, one of which is more negative and the other more positive.   In the group now under consideration oxygen, sulfur, selenium, and tellurium constitute the negative, while chromium, molybdenum, tungsten, and uranium form the positive sub-group.   In all groups the positive quality becomes more marked as the atomic weight increases.   It may thus happen that an element of a positive sub-group is more negative than one of a negative sub-group; for example, chromium is more negative than tellurium.   On the other hand, the negative quality of an element becomes more marked as the valence increases.   Sulfur with the valence VI is very strongly negative, while bivalent sulfur can barely form an acid; chromium with the valence II is decidedly positive, while hexavalent chromium is only negative.

A comparison of some of the physical constants of the chromium sub-group is exhibited in the following table:

	Chromium.	Molybdenum.	Tungsten.	Uranium.
Atomic weight..	52	96	184	239
Specific gravity........	6	8.6	18.1	18.7
Specific heat...........	0.1	0.066	0.033	0.028
Melting-point..........	above 2500°	white heat	white heat	1500°

The chemical relationship of the elements of the sub-group is quite close. The valence varies from II to VI with a tendency to form mixed compounds in which the apparent valence is III or V.

CHROMIUM.

Symbol Cr. Atomic weight 52. Valence II, IV, VI, also pseudotriad, $(Cr_2)^{VI}$. Specific gravity 6.8. Melting-point 3000°.

Occurrence.—Chromium does not occur free. The principal ore is *chrome iron*, which is a more or less pure *ferrous chromite*, $FeCr_2O_4$, or FeO,Cr_2O_3. Other native ores are *crocoisite* or lead chromate, $PbCrO_4$, and *chrome ocher*, Cr_2O_3. Traces of chromium are found in many minerals and usually give them a green color. Chromium localities are Sweden, Hungary, the United States, and the Ural Mountains.

History.—Chromium was discovered by Vauquelin in 1797. Its name means "color" and was given to the element because many of its compounds are colored.

Preparation.—Chromium may be prepared—

1. By electrolysis of a mixture of the chlorid, $CrCl_3$, and the oxid, Cr_2O_3.

2. By reduction of the oxid by means of carbon or aluminum at a very high temperature.

3. By reduction of the chlorid by metallic zinc.

Chromium is now prepared in quantities by reducing the oxid or the native chrome iron ore with carbon and lime in the electric furnace, a method discovered by Moissan in 1894. The lime prevents the formation of chromium carbid.

Pure chromium is best obtained by reducing the oxid with aluminum (Goldschmidt method).

Chromium is chiefly used in the manufacture of steel.

Physical Properties.—The physical properties of chromium depend somewhat upon the method of its preparation. When obtained by reduction of the oxid, it is a gray powder consisting of very hard, brittle, lustrous, rhombohedral crystals which have a specific gravity 6.8 and which fuse at a temperature above the melting-point of platinum (about 2500°).

Chemical Properties.—Chromium is insoluble in water and nitric acid, but dissolves in hydrochloric, acid and warm dilute sulfuric acid with evolution of hydrogen. It is unchanged in the

air, but burns brilliantly when heated in oxygen. It burns also in chlorin to form $CrCl_3$. The presence of one half of one per cent of chromium in steel makes it very hard and strong and renders it very suitable for certain purposes in the arts. The great railroad bridge at St. Louis is made of chrome steel.

CHROMIUM COMPOUNDS.

Chromium is positive and basic when bivalent, negative and acidic when hexavalent, and both basic and acidic when tetravalent. With the valence IV it does not form simple compounds, but two atoms unite together, making it seem to be trivalent; thus: $\equiv Cr—Cr\equiv$. Chromium forms two elementary positive ions, $Cr^{..}$ blue and $Cr^{...}$ purple, and one basic complex ion, $CrO^{..}$ red. $Cr^{..}$ passes readily to the more stable $Cr^{...}$ and is hence a reducing agent. The principal acid ions are Cr_2O_4'' (chromite), CrO_4'' (chromate) yellow, and Cr_2O_7'' (dichromate) red. The acid ions are oxidizing agents because they are easily reduced to the basic ions.

There is a little confusion in the naming of chromium compounds. Cr_2O_3 is called *chromic oxid*, while the salts of its hydrate are called *chromites*. This confusion arises from the twofold electric quality of chromium. There are two series of basic compounds called *chromous* and *chromic*, as the valence is II or III; so there are two acidic series called *chromites* and *chromates*, as the valence is III or VI. In addition to these there are at least three series of polychromates. Sample compounds are as follows:

		Basic.	Acidic.
Chromous sulfate,	Cr''	$CrSO_4$	
Chromic sulfate,	$(Cr_2)^{vi}$	$Cr_2(SO_4)_3$	
Zinc chromite,	$(Cr_2)^{vi}$	......	$ZnCr_2O_4 \cdot (ZnO,Cr_2O_3)$
Potassium chromate,	Cr^{vi}..............	......	K_2CrO_4
Potassium dichromate,	Cr^{vi}..............	......	$K_2Cr_2O_7$

CHROMIUM HALIDS.

Chromium Fluorid, $CrF_3,4H_2O$, is obtained by heating lead chromate, calcium fluorid, and sulfuric acid together in a leaden dish. It is a red gas which condenses to a blood-red liquid. It produces violent coughing when inhaled and is decomposed by water into HF and Cr_2O_3.

Chromous Chlorid, $CrCl_2$, is obtained by the action of hydrochloric acid upon chromium, or by gently igniting chromic chlorid

in dry hydrogen. It consists of white lustrous crystals which dissolve in water to a blue solution which is a powerful reducing agent. It absorbs oxygen from the air, becoming chromyl chlorid, $CrOCl_2$, and when treated with potassium hydroxid precipitates chromous hydroxid, CrH_2O_2.

Chromic Chlorid, Cr_2Cl_6 or $CrCl_3$, is prepared by heating an intimate mixture of chromic oxid, Cr_2O_3, and carbon in a stream of dry chlorin. The chromic chlorid sublimes over and condenses in lustrous, peach-blossom-colored scales which have a specific gravity 3.03 and are insoluble in water. When heated it dissociates so that the vapor density corresponds to the formula $CrCl_3$. It readily dissolves in water containing a small quantity of chromous, cuprous, or stannous chlorid. A similar solution is had by dissolving chromic hydroxid in hydrochloric acid. On evaporating the solution crystalline hydrates of chromic chlorid separate which contain varying quantities of water. When these crystals are heated to 250° in hydrogen chlorid or chlorin, the insoluble pink anhydrous chromic chlorid is obtained.

Chromous Bromid, $CrBr_2$, is a white crystalline solid obtained by heating chromic bromid in hydrogen, or by heating together bromin and chromium in an atmosphere of nitrogen.

Chromic Bromid, Cr_2Br_6, is obtained as dark metal-like hexagonal crystals by heating a mixture of chromic oxid, Cr_2O_3, and carbon in dry bromin vapor.

The iodids of chromium have not been prepared.

OXIDS AND HYDROXIDS OF CHROMIUM.

The oxids of chromium with the usual names are as follows:

Chromous oxid,	Cr''	CrO	$Cr{=}O$
Chromic oxid,	$(Cr_2)^{vi}$	Cr_2O_3	$O{=}Cr{-}Cr{=}O$ with O below
Chromium trioxid,	Cr^{vi}	CrO_3	$O{=}Cr{=}O$ with $\overset{\|}{O}$ below
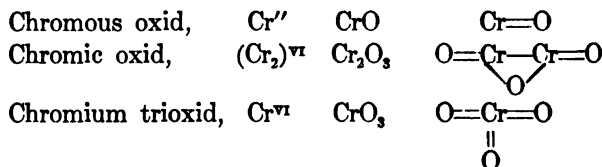
Of these oxids the first is basic and the third acidic, while the second is both basic and acidic. The oxid $Cr^{iv}O_2$ has been described, but its separate existence is still doubtful. Other oxids have been obtained with the formulas Cr_3O_4, Cr_4O_5, and Cr_5O_6. These are probably mixtures.

Chromous Oxid, CrO, has not been isolated, but **Chromous Hydroxid,** CrH_2O_2, is thrown down as a brownish-red precipitate when potassium hydroxid is added to a solution of chromous chlorid.   It is decomposed by heat as follows: $2CrH_2O_2 = Cr_2O_3 + H_2O + H_2$.

Chromous Salts.—Bivalent chromium forms salts with several of the acids.   They are formed by the action of the acids or salts upon chromium or chromous halids.   They resemble ferrous salts and are readily oxidized to chromic compounds.

Chromous Sulfate, $CrSO_4$, is obtained by dissolving chromium in sulfuric acid. It is isomorphous with ferrous sulphate and crystallizes with seven molecules of water.

Chromic Oxid, Cr_2O_3, occurs in nature as *chrome ocher,* and in combination with iron as chrome ironstone.   It is amorphous or crystalline according to the method of its preparation.

Amorphous chromic oxid is prepared—

1. By burning chromium in oxygen.
2. By igniting chromic hydroxid, trioxid, or trichlorid.
8. By heating mercurous chromate or ammonium dichromate.
4. By heating potassium dichromate with sulfur or ammonium chlorid and washing the residue with water.

Crystalline chromic oxid is obtained—

1. By passing the vapor of chromyl chlorid, $CrOCl_2$, through a red-hot tube.
2. By heating a mixture of potassium dichromate and common salt under a layer of salt and washing the residue free from chlorids.

Chromic oxid is a dull-green amorphous powder, or a mass of lustrous, dark-green hexagonal crystals, hard as corundum, and isomorphous with the corresponding oxids of iron and aluminum. It is insoluble in water and dissolves with difficulty in acids.   It dissolves in molten glass, giving it a beautiful green color, and is used in the glass and porcelain manufacture.   It is used also as a pigment under the name of *chrome green.*

Chromic Hydroxids.—While chromic oxid does not readily dissolve in water, it still forms three hydroxids as follows:

Ortho chromic hydroxid,	$Cr_2(HO)_6$	or	$Cr_2O_3,3H_2O.$
Monometa chromic hydroxid,	$Cr_2O(HO)_4$	or	$Cr_2O_3,2H_2O.$
Dimeta chromic hydroxid,	$Cr_2O_2(HO)_2$	or	$Cr_2O_3,H_2O.$

The first of these hydroxids is obtained as a light-blue precipitate when ammonia is added to a solution of a chromic salt free from fixed alkali. When dried over sulfuric acid it has the composition $Cr_2(HO)_6,4H_2O$. Dried *in vacuo* it loses three molecules of water and becomes $Cr_2(HO)_6,H_2O$. On being heated it gradually loses more water and at 200° becomes $Cr_2O_2(HO)_2$.

The second hydroxid is obtained by fusing together potassium dichromate and boric acid and washing the residue. It is called *Guignet's green* and is used as a pigment.

Chromic Salts.—The chromic hydroxids are both basic and acidic. In their basic character they act with acids to form chromic salts. Besides the simple compounds, there are numerous basic and double salts.

Chromic Sulfate, $Cr_2(SO_4)_3$, $15H_2O$, is a violet-blue solid crystallizing in small regular octahedrons. It is obtained by dissolving chromic hydroxid in sulfuric acid and letting the mixture stand in the air for some days. When heated to 100° it loses water and becomes a green solid having the composition $Cr_2(SO_4)_3,5H_2O$. On ignition the anhydrous salt is obtained.

Chromium Trioxid, CrO_3, is obtained by the action of strong sulfuric acid upon cold saturated solution of sodium or potassium dichromate:

$$H_2SO_4 + K_2Cr_2O_7 = K_2SO_4 + H_2O + 2CrO_3.$$

The crystals are drained on porous tiles, washed with nitric acid, and then freed from nitric acid by heat.

Chromium trioxid is a mass of red needle-shaped crystals which melt at 192° and decompose above 250°. Its specific gravity is 2.78. It is a strong oxidizer and is readily reduced by organic substances and other reducing agents.

ACIDS OF CHROMIUM AND THEIR DERIVATIVES.

Chromites.—Acidic chromic hydroxid forms a few compounds called *chromites*. They result from the direct union of the oxids or hydroxids:

$$ZnO + Cr_2O_3 = ZnCr_2O_4; \quad 2KOH + Cr_2O_3 = K_2Cr_2O_4 + H_2.$$

The more important of these compounds are the chromites of sodium, potassium, ammonium, zinc, iron, and manganese.

Chromic Acid, H_2CrO_4, is supposed to be formed when the tri-oxid dissolves in water, $CrO_3 + H_2O = H_2CrO_4$. On evaporating the solution the acid decomposes and the trioxid crystallizes out.

Chromates.—While chromic acid has not been isolated, its salts are quite numerous and will be described in connection with the metals which form them. The acid is dibasic, but yields only normal salts. It has a tendency also to condense two or more molecules together.

Chloro-chromic Acid, $\begin{smallmatrix}H-O\\Cl\end{smallmatrix}\!\!>\!CrO_2$, is the analogue of chlor-sulfonic acid, $\begin{smallmatrix}H-O\\Cl\end{smallmatrix}\!\!>\!SO_2$, and might be called *chlor-chromonic acid*. It has not been isolated, but its salts are well known. **Potassium chloro-chromate** is formed by the action of hydrochloric acid upon potassium dichromate, or by the action of chromyl chlorid upon potassium chlorid:

$$KCl + CrO_2Cl_2 + H_2O = 2HCl + KCrO_3Cl.$$
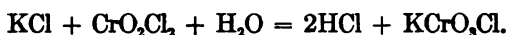
It is a red crystalline salt of specific gravity 2.5.

Chromyl Chlorid, $\begin{smallmatrix}Cl\\Cl\end{smallmatrix}\!\!>\!CrO_2$, is prepared by distilling a mix-ture of sodium chlorid, potassium dichromate, and strong sulfuric acid. It is a red, mobile, fuming liquid which boils at 118° and has a specific gravity 1.9. It dissolves iodin and chlorin and de-composes with violence in contact with water, phosphorus, sulfur, hydrogen sulfid, ammonia, alcohol, and organic matters generally. It acts as a vigorous oxidizing and chlorinating agent. When heated in a closed tube, it is converted into trichromyl chlorid, $Cr_3O_6Cl_2$, a black amorphous deliquescent powder. Fluo, bromo, and iodo chromates. as well as chromyl fluorid, have been described.

Perchromic Acid.—When hydrogen peroxid is added to a dilute aqueous solution of chromium trioxid, or to a solution of potassium dichromate acidulated with sulfuric acid, a deep-blue solution is obtained. This blue substance has been called *perchromic acid* and the formula $HCrO_4$ has been assigned to it. It is more probably a molecular compound of hydrogen peroxid and chromium trioxid in varying proportions, possibly, $H_2O_2,2CrO_3$. When diluted with water, or when evaporated oxygen is given off, chromium trioxid is formed and the blue color disappears. With alkalies alkaline

chromates are formed with the evolution of oxygen. The formation of this compound affords a delicate test for chromic acid and hydrogen peroxid.

Illustration.—To an acidulated solution of potassinm dichromate add some hydrogen peroxide and shake the blue solution with ether. The ethereal solution is beautifully colored, but the color soon fades.

Dichromic Acid, $H_2Cr_2O_7$, is theoretically obtained by taking a molecule of water from two molecules of chromic acid. It exists only in solution and has not been isolated.

Dichromates are formed by the action of acids upon chromates. They are colored, crystalline salts mostly soluble in water. Potassium dichromate, $K_2Cr_2O_7$, is the one of greatest importance.

Chromate and Dichromate Ions.—The yellow chromate ion is converted by hydrogen ion into the red dichromate ion as follows:

$$2CrO_4'' + 2H\cdot = Cr_2O_7'' + 2HO'.$$
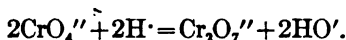
It is for this reason that chromates are changed into dichromates by acids. Even a water solution of a chromate undergoes this change by hydrolysis and becomes alkaline:

$$2CrO_4'' + H_2O = Cr_2O_7'' + 2HO'.$$
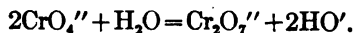
Both reactions are reversible and a dichromate solution may be acid:

$$Cr_2O_7'' + H_2O = 2CrO_4'' + 2H\cdot.$$
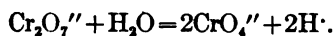
A water solution of either chromate or dichromate will therefore contain both chromate and dichromate ions.

CHROMIUM WITH THE SULFOIDS AND NITROIDS.

Chromium forms several compounds with sulfur and two with selenium. It does not unite to nitrogen, but forms phosphid, carbid, and silicid, which resemble the corresponding compounds of iron.

MOLYBDENUM.

Symbol Mo. Atomic weight 96. Valence II, IV, VI. Specific gravity 8.6.

Occurrence.—Molybdenum does not occur free upon the earth. The spectroscope shows it to exist in the sun. The principal ore is *molybdenite*, MoS_2. Other native compounds are *wolfenite*, $PbMoO_4$, *pateraite*, $CoMoO_4$, and *molybdic ocher*, MoO_3. It is also found in

small quantities in many iron ores. The chief localities are Sweden, Norway, Bohemia, and the New England States.

History.—The word molybdenum is from the Greek and means *lead*. The term was applied in earlier times to any mineral which had a lead-like appearance, such as galena (lead sulfid), graphite, antimony sulfid, and molybdenum sulfid. The element was first separated by Hjelm in 1782.

Preparation.—Molybdenum is prepared by reducing the trioxid or the chlorids at a red heat in a current of hydrogen, or by strongly heating the trioxid with carbon in a graphite crucible. To obtain molybdenum from the ores, they must first be oxidized to the trioxid by roasting in the air.

Properties.—Molybdenum is silver white, lustrous, very hard, and almost infusible, and has a specific gravity 8.6. It is insoluble in water, and in hydrochloric, hydrofluoric, and dilute sulfuric acids; soluble in strong sulfuric acid, nitric acid, aqua regia, and potassium hydroxid. It combines directly with oxygen, chlorin, and bromin, but not with iodin. It is unchanged in the air, but when heated tarnishes and burns to MoO_3. It forms alloys with aluminum, copper, platinum, gold, and silver.

MOLYBDENUM COMPOUNDS.

Molybdenum, like chromium, is mainly basic with the valences II and IV, but strongly acidic with the valence VI. In its positive character it forms few compounds except with the negative elements. With these it enters into many double combinations. As a hexad it forms the molybdic acids, of which there are numerous complex derivatives. Indeed, no other acid has so many derivatives unless it be silicic acid. A description of the molybdates alone would fill a small volume.

The only compounds of commercial importance are molybdenum trioxid, MoO_3, and ammonium tetramolybdate, $(NH_4)_2Mo_4O_{13}$, which are used in analytic chemistry in the determination of phosphorus in phosphates, fertilizers, and irons.

MOLYBDENUM HALIDS AND OXYHALIDS.

Fluorids.—Molybdenum hexafluorid, MoF_6, is obtained by passing fluorin gas over molybdenum at 60° and condensing the product at −70°. It is a white solid which melts at 17° and boils at 35°. The oxyfluorid, MoO_2F_2, is obtained by heating MoO_3 with metallic fluorids. $MoOF_4$ is obtained by heating $MoOCl_4$ with anhydrous HF.

Chlorids.—The following chlorids have been prepared:

Molybdenum dichlorid, $MoCl_2$, a bright-yellow, non-volatile powder.

Molybdenum trichlorid, $MoCl_3$, a dark reddish-brown powder.

Molybdenum tetrachlorid, $MoCl_4$, a brown, deliquescent solid.

Molybdenum pentachlorid, $MoCl_5$, a black, crystalline solid.

Oxychlorids.—The oxychlorids are as follows:

Brown oxychlorid, $Mo_2O_3Cl_5$; *violet oxychlorid,* $Mo_2O_3Cl_4$; *yellow oxychlorid,* MoO_2Cl_2: *green oxychlorid,* $MoOCl_4$.

There are several *hydroxychlorids,* of which $Mo(OH)_2Cl_2$ and $Mo_2(OH)_2Cl_4$ may be taken as examples.

Bromids.—Three molybdenum bromids are formed by the direct union:

Molybdenum dibromid, $MoBr_2$, a yellow powder.

Molybdenum tribromid, $MoBr_3$, dark-green crystals.

Molybdenum tetrabromid, $MoBr_4$, black, lustrous needles.

There is one *oxybromid,* MoO_2Br_2, yellow deliquescent crystals.

The *hydroxybromids* are similar to the hydroxychlorids.

Mixed Halids.—Among the mixed halids of molybdenum are:

Molybdenum fluobromid, $Mo_2F_2Br_4,3H_2O$.

Molybdenum chlorotetrabromid, $Mo_2Cl_2Br_4,3H_2O$.

Molybdenum chlorobrom hydroxid, $Mo_3Cl_4Br(OH),2H_2O$.

Molybdenum iodochlorid, $MoI_2Cl_4,3H_2O$.

Molybdenum iodobromid, MoI_2Br_4.

OXIDS AND HYDROXIDS OF MOLYBDENUM.

Oxids.—Four oxids of molybdenum have been isolated.

Molybdenum monoxid, MoO, a brown powder.

Molybdenum sesquioxid, Mo_2O_3, a black or yellow solid obtained by reducing MoO_3 with hydrogen or zinc.

Molybdenum dioxid, MoO_2, a dark-brown powder also obtained by reducing MoO_3.

Molybdenum trioxid, MoO_3, formed by burning molybdenum, or by roasting MoS_2 in the air. It is a light, white solid of specific gravity 4.39. It sublimes when heated and melts at a red heat. It dissolves in 500 parts cold and in 960 parts hot water. The solution has a metallic, acid taste. It dissolves in acids and alkalis.

Hydroxids.—The first three oxids of molybdenum form basic hydroxids. They dissolve in acids, forming salts which are not very well defined.

Molybdous hydroxid, $Mo(OH)_2$, is formed by treating $MoBr_2$ with KHO.

Molybdic hydroxid, $Mo_2(OH)_6$, is a black solid obtained by treating $MoCl_3$ with hydrochloric acid and zinc.

A variable hydroxid of molybdenum dioxid is obtained by treating the pentachlorid with ammonia.

MOLYBDIC ACID AND THE MOLYBDATES.

Molybdic Acid, H_2MoO_4.—The only acid of molybdenum is the one formed by hydrating the trioxid. There are many hydrates, either real or hypothetical, which give rise to complex salts. The simplest one is the common molybdic acid, H_2MoO_4. This compound is precipitated when ammonium molybdate is gently heated for a long time, or when it is treated with nitric acid. It forms a mass of minute needle-shaped crystals and is quite insoluble in water. It is the dimeta acid and by further hydration the monometa and ortho acids, H_4MoO_5 and H_6MoO_6, are formed.

Molybdates.—There are normal, double, acid, and basic molybdates not only of the above acids, but of other hypothetical acids formed by the union and condensation of two or more molecules of molybdic acid. The latter are called polymolybdates. They have a structure similar to that of the polychromates. A few examples are: Barium molybdate, $BaMoO_4$; sodium dimolybdate, $Na_2Mo_2O_7$; calcium trimolybdate, $CaMo_3O_{10},6H_2O$; magnesium tetramolybdate, $MgMo_4O_{13},19H_2O$; sodium hydrogen octomolybdate, $NaHMo_8O_{25},4H_2O$.

Furthermore, not only does the molybdic-acid molecule multiply itself, but it has at the same time the faculty of uniting to other elements and molecules to form numerous compounds of great complexity. There are antimono, arseno, fluo, phospho, silico, vanado, phosphovanado, phosphostanno, alumino, ferro, chromo, auro, and mangano molybdates. In these compounds the number of molybdenum atoms may run to 72 or even higher. The general formula for one series of phosphomolybdates is $mMoO_3,2P_2O_5,nR_2O,xH_2O$, in which m is any even number from 2 to 48, n is generally 6, but may be as low as 2, and as high as 14, and x may run from 24 to 46.

Fluomolybdates.—Salts are obtained by dissolving molybdates in hydrofluoric acid. The structure of these compounds will be understoood from the formula of potassium fluomolybdate,

$$\begin{array}{c} K{-}F{=}F \\ K{-}F{=}F \end{array}\!\!\bigg\rangle MoO_2.$$
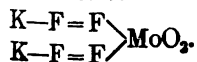
MOLYBDENUM WITH SULFUR AND SELENIUM.

The following compounds are described:

Molybdenum disulfid, MoS$_2$, a black, lustrous powder obtained by heating a mixture of molybdenum trioxid and sulfur.

Molybdenum trisulfid, MoS$_3$, a black powder obtained by passing H$_2$S through a solution of a molybdate, then adding hydrochloric acid.

Molybdenum tetrasulfid, MoS$_4$, a cinnamon-brown powder obtained by heating MoS$_3$ to 100° in H$_2$S.

Molybdenum diselenid, MoSe$_2$, a bluish-gray solid obtained by saturating acid ammonium molybdate with H$_2$Se.

Thiomolybdates.—Several thiomolybdic acids and many thiomolybdates are known. There are two classes of these compounds, in one of which all the oxygen is replaced by sulfur, while the others contain both oxygen and sulfur. Examples are potassium thiomolybdate, K$_2$MoS$_4$, and sodium oxymonothiomolybdate, Na$_2$MoO$_3$S.

TUNGSTEN (WOLFRAM).

Symbol W. Atomic weight 184. Valence II, IV, VI. Specific gravity 19.13.

Occurrence.—Tungsten does not occur free. It is found combined in the minerals *wolframite*, (FeMn)WO$_4$, *Scheelite*, CaWO$_4$, *Stolzite*, PbWO$_4$, and *tungstite* or *tungstic ocher*, WO$_3$. It is often associated with iron, manganese, tin, and copper. The principal localities are Cornwall, England, Munroe, Conn., and the gold regions of North Carolina and Nevada.

History.—The word Tungsten is from the Swedish and means *heavy stone*. The name was applied to the mineral Scheelite or calcium tungstate. In 1781 Scheele proved that the mineral was composed of lime and a peculiar acid. In 1783 the Spanish chemists Juan, José, and Fausto d'Elhujar obtained the same acid from the mineral wolfram (iron-manganese tungstate), and also separated the element, which was called *wolfram*, whence the symbol W.

Preparation.—Tungsten is prepared by reducing the trioxid with hydrogen or carbon, or by reducing the chlorids in the vapor of sodium.

Properties.—Tungsten is a hard, brittle, gray, crystalline powder with metallic luster and specific gravity 19.13. It does not tarnish

in the air or oxygen, but burns at a red heat to WO_3.   It combines at high temperatures with chlorin, bromin, and iodin.   It is oxidized by nitric acid, but is scarcely attacked by hydrochloric or sulfuric acid; dissolves slowly in alkali hydroxids.   It forms alloys with various metals.

TUNGSTEN COMPOUNDS.

The tungsten compounds are exactly analogous to those of chromium and molybdenum. A few only need be mentioned.

Halids and Oxyhalids.—The following halids and oxyhalids are described:

Tungsten fluorid has not been isolated, though it is probably formed when the trioxid dissolves is hydrofluoric acid.   ⟍

Tungsten dichlorid, WCl_2, a gray, amorphous powder.

Tungsten tetrachlorid, WCl_4, soft, crystalline, gray powder.

Tungsten pentachlorid, WCl_5, black needle-shaped crystals.

Tungsten hexachlorid, WCl_6, dark violet or steel-blue crystals.

Tungsten monoxychlorid, $WOCl_4$, red needle shaped crystals.

Tungsten dioxychlorid, WO_2Cl_2, lemon-yellow scales.

Tungsten dibromid, WBr_2, black velvety solid.

Tungsten pentabromid, WBr_5, violet-brown needles.

Tungsten monoxybromid, $WOBr_4$, black shining needles.

Tungsten dioxybromid, WO_2Br_2, red transparent crystals.

Tungsten diiodid, WI_2, green metal-like solid.

Oxids.—There are only two definite oxids of tungsten:

Tungsten dioxid (Brown oxid), WO_2, is prepared by reducing the trioxid with hydrogen at a red heat, or with zinc and hydrochloric acid. It is a brown or copper-red powder, of specific gravity 12.1. It dissolves slightly in hydrochloric and sulfuric acids, yielding purple solutions. It oxidizes readily to WO_3. It forms no hydrate.

When WO_3 is partially reduced it forms the substance called the *blue oxid* of tungsten. It is a mixture of varying composition intermediate between WO_3 and WO_2.

Tungsten trioxid, WO_3, occurs native as *tungstic ocher*. It may be prepared by burning tungsten, or by heating ammonium or mercurous tungstate or tungstic acid. It is a canary-yellow powder, amorphous or crystalline, of specific gravity 6.84. When heated in a current of hydrogen it is reduced first to the blue oxid, then to the brown oxid, and finally to pure tungsten. It is insoluble in water and acids, but dissolves in fixed alkalies and ammonia.

Tungstic Acid, H_2WO_4.—This compound is obtained when a tungstate is treated with hot acid in excess. It is a yellow amorphous powder nearly insoluble in water and the acids except hydrofluoric.

The acid H_4WO_5 is obtained when an alkali tungstate is treated with an acid in the cold. It is a white, bitter solid soluble in water, but insoluble in most acids.

Several other acids have been separated, among which the most important is the so-called *metatungstic* or *tetratungstic* acid, $H_2W_4O_{13},7H_2O$, formed by the decomposition of the barium salt with sulfuric acid or the lead salt with hydrogen sulfid. It is a crystalline, yellow powder, soluble in water.

Tungstates.—There are numerous tungstates and polytungstates which are analogous to the corresponding compounds of molybdenum, and need not be treated in detail. While the basicity of the molybdates is generally two, that of the tungstates tends to rise along with the number of tungsten atoms. We have for example, sodium tungstates as follows: $Na_2W_2O_7$, $Na_4W_3O_{11}$, $Na_6W_7O_{24}$, $Na_{10}W_{12}O_{41}$, etc.

Tungsten Bronzes.—Alkali tungstates combine with tungsten dioxid to form beautifully colored substances which have been used as substitutes for bronze powders. Examples are *sodium tungsten bronze*, $Na_2W_2O_7,WO_2$, and *potassium tungsten bronze*, $K_2W_2O_7,WO_2$.

Sulfids and Selenids.—Two sulfids and one selenid are described:

Tungsten disulfid, WS_2, soft, black acicular crystals.
Tungsten trisulfid, WS_3, a black powder.
Tungsten selenid, WSe_2, a gray solid.

Thiotungstates.—The thiotungstates are formed by dissolving tungsten trisulfid in alkali hydrosulfids. Common examples are *potassium thiotungstate*, K_2WS_4, and *ammonium oxydithiotungstate*, $(NH_4)_2WS_2O_2$.

URANIUM.

Symbol U. Atomic weight 239. Valence IV, VI, VIII. Specific gravity 18.33.

Occurrence.—Uranium is a rare element not found free. Its principal ore is pitch blend, which is an impure uranoso-uranic

oxid, U_3O_8, found in Cornwall, England, in several European localities, and in North Carolina and Connecticut.

History.—Klaproth, in 1798, found in the mineral *pitch blend* a peculiar metal to which he gave the name *uranium*, after the planet Uranus, which Herschel had discovered a few years before. The body which he obtained was the oxid of uranium, and it was not until 1842 that the metal was really separated by Péligot.

Preparation. — The preparation of uranium from its ores involves a rather complicated process. In small quantity it may be obtained by the action of potassium or sodium upon uranous chlorid, UCl_4.

Properties.—Uranium is a hard, malleable, nickel-white solid of specific gravity 18.33. It does not tarnish in the air, but burns brightly when heated, forming the green oxid U_3O_8. It unites directly with chlorin and sulfur when heated with them. It is soluble in nitric and hydrochloric acids, but not in alkalis. It generally contains more or less of radium and emits what are known as uranium rays.

URANIUM COMPOUNDS.

The compounds of uranium are very similar to those of molybdenum and tungsten, but have many special peculiarities. There are uranous, uranic, and peruranic compounds as the valence is IV, VI, or VIII. The uranium ion $U^{....}$ has a fine green color, and there is a basic uranyl ion $UO_2^{..}$ which is yellow with a green fluorescence. Complex ions are numerous.

Halids.—These compounds are mostly tetrahalids. Uranium unites directly with fluorin, chlorin, and bromin, but not with iodin. The compounds UF_4, UCl_4, UBr_4, and also U_2Cl_5, and UCl_5, have been prepared.

Oxids and Hydroxids. — Uranium forms three definite oxids, the first basic, the second basic and acidic, and the third acidic.

Uranous oxid, UO_2, is obtained by reducing the green oxid U_3O_8, or uranic oxalate in a current of hydrogen. It is a brown or red powder of specific gravity 10.15. It readily oxidizes to U_3O_8

Uranous hydroxid, $U(HO)_4$.—When an alkali is added to a solution of a uranous salt, a green precipitate falls of $U(HO)_4$ which turns reddish brown because of slow oxidation. It dissolves in acids, forming green uranous salts, of which uranous sulfate, $U(SO_4)_2$, is an example.

Uranic oxid, UO_3, or *Uranyl oxid*, $(UO_2)O$, is obtained as a brownish-yellow powder by heating uranyl hydroxid or nitrate.

Uranyl hydroxid, $UO_2(HO)_2$, or *Uranic acid*, H_2UO_4, is obtained by gently heating the nitrate. It is a yellow solid of specific gravity 5.92. It is both basic and acidic, forming uranyl salts and uranates.

Uranyl salts.—The bivalent radical UO_2 acts like a positive element to form salts. These are usually yellow, and when made a constituent of glass impart to it a beautiful fluorescence. Examples are the uranyl halids, UO_2F_2, UO_2Cl_2, UO_2Br_2, and uranyl sulfate, UO_2SO_4.

Uranyl forms with phosphoric acid the salt UO_2HPO_4, insoluble in acetic acid. In the presence of ammonia the compound $UO_2(NH_4)PO_4$ is formed. This action is used in the volumetric estimation of phosphoric acid. Acetic acid and ammonium acetate are added to the phosphoric acid solution and a solution of uranyl nitrate, $UO_2(NO_3)_2,6H_2O$, of known strength is added until a drop of the solution gives a red color with potassium ferrocyanid (uranyl ferrocyanid).

Uranates.—Uranates are precipitated by alkalis from solutions of uranic or uranyl salts. The diuranates are the most common, though many complex polyuranates are known.

Uranoso-uranic oxids.—Uranous and uranic oxids form various mixtures, of which the two following are the best known :

Black oxid of uranium, U_3O_8, or UO_2,UO_3, used for painting on porcelain.

Green oxid of uranium, U_3O_8, or $UO_2,2UO_3$, found in pitch blend.

Peruranic oxid and acid.—White crystalline *peruranic oxid*, UO_4, and yellow tetrabasic *peruranic acid*, H_4UO_6, are known but have not been well studied.

Peruranates.—These compounds are formed by oxidizing the uranates with hydrogen peroxid. Examples are sodium peruranate, $Na_4UO_8,8H_2O$, and uranyl sodium peruranate, $(UO_2)Na_2UO_8,6H_2O$.

Uranium and Sulfur.—Several compounds of uranium and sulfur have been described. Only two need be mentioned here :

Uranous sulfid, US_2, an amorphous, dark-gray powder obtained by heating uranium in sulfur vapor.

Uranyl sulfid, UO_2S, precipitated by ammonium sulfid from a solution of uranyl nitrate.

CHAPTER XXVI.

GROUP V B. THE NITROIDS. NITROGEN GROUP.

Nitrogen 14. Phosphorus 31. Arsenic 75. Antimony 120. Erbium 166. Bismuth 208.

In the members of this group we have again a fine illustration of the gradation of properties characteristic of the periodic system.

In electric quality nitrogen is extremely negative and bismuth decidedly positive, while arsenic and antimony are both negative and positive and are sometimes called *metalloids*.

As to valence, these elements are normally triads, but the valences one and five are usually found. With nitrogen particularly and to a certain extent with phosphorus the valence does not seem to be very definite. Nitrogen exhibits successively the valences I, II, III, IV, and V.

In physical properties the gradation is well marked. As the atomic weight increases, the specific gravity increases, and the metallic character also. The compounds of arsenic, antimony, and bismuth are isomorphous. Some of the physical constants are shown in the following table:

	Nitrogen.	Phos-phorus.	Arsenic.	Anti-mony.	Erbium.	Bismuth.
Atomic weight........	14	31	75	120	166	208
Specific gravity.......	0.885 (Liq.)	1.82	5.7	6.7		9.8
Density...............	14	62	150			
Specific heat.........		0.202	0.083	0.058		0.031
Melting-point.........	− 193°	45°	500°	425°		270°
Atoms in mol........	2	4	4			

The elements of this group form many similar compounds, the chief differences being due to the increasing positive character as we go towards bismuth. Nitrogen forms strong acids, while bis-

muth is almost wholly basic. The hydrogen compounds are all alkaline, while those of groups seven and six are acid in character. The chlorine compounds are unstable and vigorous chemical agents.

<div style="text-align:center">● NITROGEN.</div>

Symbol N. Atomic weight 14. Molecular weight 28. Valence I, III, V. Density 14. Liter weighs at 0° and 760 mm. 1.257.

Occurrence.—Nitrogen occurs free in the air, of which it forms about four fifths, and in solution in all terrestrial waters. The spectroscope shows it to exist in some nebulæ and probably in the sun. The gas in the swim-bladder of fishes is mostly nitrogen.

Combined nitrogen occurs in many minerals, chiefly as nitrate, and it is an essential constituent of the protoplasmic and albuminous portions of the bodies of all plants and animals. The principal native compounds are *niter* or *saltpeter*, KNO_3, and *ammonium nitrate*, NH_4NO_3, which are very widely distributed; and *sodium nitrate* or *Chile saltpeter*, which is found in large deposits in Chile.

History.—In 1772, Dr. Rutherford of Edinburgh showed that after air had been breathed for some time by an animal, and the carbon dioxid removed by potassium hydroxid, there remained a gas which supported neither life nor combustion. He called it *mephitic air*. Scheele showed that this gas was a constituent of the atmosphere and Lavoisier demonstrated that the air was composed mainly of two gases, one of which supports life and combustion, while the other does not. To the latter he gave the name *azote*, which means *not supporting life*. This name is still used in France. The name *nitrogen* (niter maker) was given by Chaptal to the element because it was found to be a constituent of niter (KNO_3).

Preparation.—Nitrogen is most simply obtained from the air by removal of the oxygen. This may be done in several ways:

1. By burning phosphorus in confined air. The phosphorus combines with the oxygen to form solid P_2O_5 and the nitrogen remains mixed with small quantities of other gases (carbon dioxid and argon).

2. By passing air over heated copper. The copper unites to the oxygen to form copper oxid, CuO, and the nitrogen passes on.

3. By shaking air with a solution of cuprous chlorid in hydrochloric

acid. The oxygen is absorbed with the formation of water and cupric chlorid :

$$Cu_2Cl_2 + 2HCl + O = H_2O + 2CuCl_2.$$
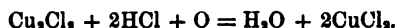
Chemically nitrogen may be prepared in many ways:

1. By heating ammonium nitrite or a mixture of ammonium chlorid and sodium nitrite:

$$NH_4NO_2 + 2H_2O + N_2;$$
$$NH_4Cl + NaNO_2 = NaCl + 2H_2O + N_2.$$
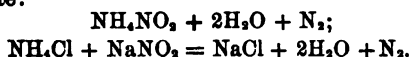
2. By heating ammonium nitrate with ammonium chlorid :

$$2NH_4NO_3 + NH_4Cl = Cl + 6H_2O + 5N.$$
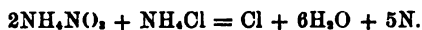
3. By heating ammonium dichromate or a mixture of potassium dichromate and ammonium chlorid:

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

4. By decomposing ammonia with chlorin :

$$2NH_3 + 6Cl = 6HCl + N_2.$$

For lecture purposes nitrogen may be prepared by floating a bit of phosphorus on a flat cork in a basin of water, igniting it, and inverting over it a cylinder. The water dissolves the phosphoric oxid and rises in the vessel as the oxygen is consumed. When the action is finished, the mouth of the cylinder is closed with a glass plate and the cylinder inverted.

A purer nitrogen is obtained by aspirating air through a tube containing copper heated to redness. The air should be passed through tubes containing potassium hydroxid and sulfuric acid to remove carbon dioxid and moisture. If dry nitrogen is desired, the air may be driven from a gas-holder and the nitrogen dried with sulfuric acid and collected over mercury.

To prepare nitrogen by the chemical reactions, heat the materials in a flask furnished with a delivery-tube and collect the nitrogen over water.

In preparing nitrogen by the action of chlorin on ammonia, pass the chlorin from the generating flask first through water, then into the bottle containing strong aqueous ammonia, and collect the nitrogen over water. In this operation care must be taken to have the ammonia always in excess, otherwise the highly explosive and dangerous nitrogen chlorid may be formed.

Physical Properties.—Nitrogen is a colorless, odorless, tasteless gas of specific gravity 0.971 (air = 1). Its density is 14, and therefore the molecule contains two atoms. One hundred volumes of

water dissolves 2 volumes of nitrogen at 0° and 1.5 volumes at 13°. It is more soluble in alcohol, 100 volumes dissolving 12 volumes.

The critical temperature and pressure of nitrogen are − 146.3° and 35 atmospheres. Liquid nitrogen is limpid and colorless, or slightly blue, and has a specific gravity 0.885. It boils at − 193° and freezes at − 214°.

Chemical Properties.—Free nitrogen is one of the most inactive of all the elements. It does not burn, and supports neither respiration nor combustion. It combines directly with very few elements. At the high temperature of the electric spark it unites slowly with oxygen or hydrogen. It combines at a red heat with a few metals, such as magnesium and lithium. Nearly all its compounds are unstable and chemically active. It is a constituent of gunpowder, nitroglycerin, and most explosives. Its valence is indifferent, ranging from one to five, and it readily changes valence in passing from one compound to another, as when ammonia and hydrogen chlorid unite, $N'''H_3 + HCl = N^vH_4Cl.$ •

Illustrations.—The effect of nitrogen upon combustion is shown by lowering a lighted taper in a vessel of the gas.

The union of nitrogen with oxygen may be shown by passing electric sparks through a confined portion of air. A eudiometer tube may be used. Red fumes of the oxid soon appear. If the open arm of the tube be filled with mercury the action is aided by the pressure.

Physiological Properties.—Nitrogen passes in and out of the lungs without effect. When pure nitrogen is breathed, it produces suffocation and asphyxia from simple want of oxygen.

Uses.—The principal use of free nitrogen is to dilute the oxygen of the air and thus diminish its activity.

Tests.—There is no special test for free nitrogen. It may generally be recognized by its inactivity.

NITROGEN COMPOUNDS.

Nitrogen is chemically inactive and its compounds are all unstable. It unites with most of the non-metals and with but few of the metals. It has a strong tendency to form radicals, especially with hydrogen, oxygen, and carbon, and in this way enters into an immense number of compounds. These radicals separate readily as active ions, and thus nitrogen compounds are among the most energetic of chemical agents.

COMPOUNDS OF NITROGEN WITH HYDROGEN.

There are five combinations of nitrogen with hydrogen, two of which are univalent radicals which act like elements and form numerous compounds. They have names and formulas as follows:

Ammonia,	$N'''H_3$	$H-\overset{\overset{\textstyle H}{\mid}}{N}-H$
Ammonium,	$(N^vH_4)'$	$\overset{H}{\underset{H}{>}}N\underset{\mid}{\overset{\mid}{<}}\overset{H}{\underset{H}{}}$
Amidogen,	$(N'''H_2)'$	$\overset{H}{\underset{H}{>}}N-$
Hydrazin,	$N_2'''H_4$	$\overset{H}{\underset{H}{>}}N-N\overset{H}{\underset{H}{<}}$
Hydrazoic acid,	$N_3'''H$	$\overset{N}{\underset{N}{\|}}{>}N-H$

AMMONIA.

Formula NH_3. Molecular weight 17. Density 8.5. Liter weighs at 0° and 760 mm. 0.76 grams.

Occurrence.—Ammonia scarcely occurs free because of its strong disposition to unite to water and carbon dioxid to form the hydroxid and the carbonate. As the hydroxid and as ammonium salts (carbonates, nitrates, nitrites, sulfates, and chlorids) it is widely distributed in small quantities in atmosphere, waters, and soils. It comes from the fumaroles in the volcanic regions in Tuscany, and considerable deposits of the chlorid and sulfate are found in the vicinity of active volcanoes. Ammonium compounds are always formed in the decomposition of nitrogenous organic matters.

History.—Ammonium chlorid was known to Geber in the seventh century. It was brought from Armenia and called *sal armenicum*. This name was changed to *sal armonicum*, and finally to *sal ammonicum*. The last name was applied to the salt which came from the vicinity of the temple of Jupiter Ammon in the Libyan desert. Aqueous ammonia was afterwards prepared by distilling hoofs and horns of animals and thereby got the name *spirits of hartshorn*.

Ammonia was distinguished from ammonium carbonate by Black in 1756. Priestley, in 1774, collected it over mercury and called it *alkaline air*. Berthollet determined its composition in 1785 by decomposing it with the electric spark. The name *ammonia* was given to the gas in 1783.

Preparation.—Ammonia is obtained—

1. By the direct union of its elements brought about by means of the silent electric discharge.

2. By decomposition of ammonium salts by heat, or by alkaline hydroxids aided by heat : $Ca(HO)_2 + 2N_4HCl = CaCl_2 + H_2O + 2NH_3.$

3. By the action of nascent hydrogen upon nitrites and nitrates, as when metals act upon these compounds in the presence of caustic alkalis:

$$NaNO_3 + 4H_2 = NaHO + 2H_2O + NH_3.$$

4. By the putrefaction, decay, and dry distillation of organic substances, and especially of coal. It is largely produced as a by-product of the gas manufacture, and most of the ammonia and ammonium compounds of commerce come from this source.

For lecture purposes ammonia is most conveniently prepared by gently heating the strong aqueous solution or a mixture of slaked lime and ammonium chlorid. The gas is dried by passing over quicklime. It is collected by displacement in inverted vessels or over mercury, or is conducted into water to form the solution.

Physical Properties.—Ammonia is a colorless gas with a very pungent odor and a burning alkaline taste. It is lighter than air, its density being 8.5 and its specific gravity 0.589 (air = 1). Its index of refraction is 1.3 (air = 1).

Ammonia is very soluble in water, alcohol, and ether. One volume water at 0° dissolves more than 1100 volumes of the gas. The solution is attended with the evolution of heat, and when the gas is expelled from the water heat is absorbed. By passing a current of air through a strong solution the temperature may be lowered even to $-40°$. The solubility diminishes as the temperature increases until at 100° it is 0. As the gas dissolves, the water expands so that the specific gravity diminishes as the strength of the solution increases. The solution saturated at 14° has a specific gravity 0.884 and contains 36 per cent NH_3. The specific gravity of a 30 per cent solution is 0.898, 20 per cent 0.925, and 10 per cent 0.959. The strongest commercial ammonia has a specific gravity 0.886

and contains 35 per cent NH_3. The weaker ammonia contains about 10 per cent NH_3.

Ammonia is rather easily liquefied. Under a pressure of 7 atmospheres at 16°, or 4.2 atmospheres at 0°, or under ordinary pressure at − 40°, it becomes a colorless, mobile, highly refractive liquid of specific gravity 0.623 at 0°. The liquid boils at − 33.7° and solidifies at − 75°. The vapor tension is 4.4 atmospheres at 0°, 6.9 at 15.5°, and 10 at 28°. The critical temperature and pressure are 130° and 114 atmospheres. On allowing the liquid to evaporate, intense cold is produced. The liquid dissolves the alkali metals, making a blue solution, which on evaporation leaves the metals unchanged.

Illustrations.—To show the cold produced by the evaporation of ammonia put 100 cc. of the strongest solution in a small flask, place the flask on a block of wood wet with water and blow through the solution a rapid current of air. In a few minutes the flask will be found frozen to the block.

Chemical Properties.—Ammonia is chemically quite active. It acts like a bivalent radical uniting directly to other compounds. It is decomposed by a red heat and by the electric spark. It does not support combustion and is incombustible in the air, but burns in oxygen, in chlorin, and in bromin vapor. Burning in oxygen, it yields water and nitrogen, together with some ammonium nitrite and nitrogen tetroxid. A mixture of oxygen and ammonia is explosive. It acts vigorously with the halogens giving the ammonium halid and free nitrogen, $4NH_3 + 3Cl = 3NH_4Cl + N$. Acting with chlorin in excess the highly explosive nitrogen chlorid NCl_3 is formed. Alkali metals replace one of the hydrogen atoms (NH_2K), and at a red heat all three (K_3N). It unites directly with water to form ammonium hydroxid, and with acids to form ammonium salts.

The water solution of ammonia contains ammonium hydroxid, NH_4OH. This compound is alkaline, caustic, and quite active, and is called the *volatile alkali*. It is not highly dissociated and is therefore a weak base. The dissociation in the decinormal solution is 1.5 per cent, in the twentieth-normal 6 per cent, and in the hundredth-normal 13 per cent.

The heat of formation of ammonia is $(N,H_3) = 11,800$ cal.; the heat of solution is $(NH_3,Aq.) = 8800$ cal.; and the total heat of formation and solution is $(N,H_3,Aq.) = 20,600$ cal.

Illustrations.—The combustion of ammonia in oxygen may be thus shown:

1. Lower a jet of ammonia in a jar of oxygen, bringing it in contact with a flame just as it enters.

2. Let oxygen bubble through a warmed solution of ammonia in an open flask and ignite the escaping gases.

3. Connect with a flask, in which ammonia solution is being heated, a glass jet and surround it with a tube through which oxygen is made to pass from below. On bringing a flame to the jet the ammonia burns in the oxygen.

A jet of ammonia lowered in chlorin ignites and continues to burn.

The decomposition of ammonia by heat may be shown by passing the gas through a tube heated to redness and collecting the gases over water.

The decomposition by electricity may be shown by filling a eudiometer half full of ammonia and passing electric sparks. The volume of gas doubles.

To show the affinity of ammonia for acids fill two cylinders, the one with ammonia and the other with hydrogen chlorid, and bring them mouth to mouth. The cylinders become suddenly filled with dense white fumes of ammonium chlorid. A few cubic centimeters of the aqueous solutions may be used instead of the gases.

To show the action of alkali metals upon ammonia introduce a fragment of potassium into a bulb-tube which terminates at one end in a small aperture. Pass a stream of ammonia and heat the bulb. The potassium bursts into flame and burns in the ammonia, while the liberated hydrogen may be ignited at the end of the tube.
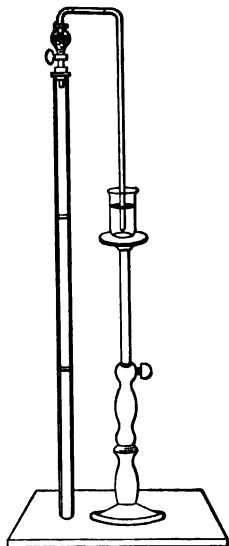
Fig. 61.

The volumetric composition, and at the same time the action with chlorin, may be shown as follows: To a tube about a meter long and closed at one end is fitted a cork carrying a dropping-funnel, or the tube itself may be furnished with stop-cock and funnel. The tube is filled with chlorin and a few cc. of strong ammonia placed in the funnel. The ammonia is admitted drop by drop through the stop-cock. When the action is complete, water acidulated with sulfuric acid is added through the funnel until equilibrium is restored. This will be when the tube is two thirds full of the liquid. The residue is nitrogen. The three volumes of chlorin have united to three volumes of hydrogen and left one volume of nitrogen.

Physiological Properties.—Ammonia is stifling and irritating to the respiratory organs. It is caustic and disorganizes the mucous membrane. It is not poisonous. It is seldom taken internally, but applied to the skin it has cleansing and curative effects.

Uses.—The uses of ammonia are very numerous, both in the arts and in chemical laboratories. Its usefulness in chemical operations is largely due to the fact that it is a strong alkali and at the same time volatile, leaving no residue when evaporated. One of its most important uses is in the manufacture of ice. Its use for this purpose is based upon—

1. Its extreme solubility.
2. Its expulsion from solution by heat.
3. Its easy liquefaction.
4. The great cold produced by its return from the liquid to the gaseous state.
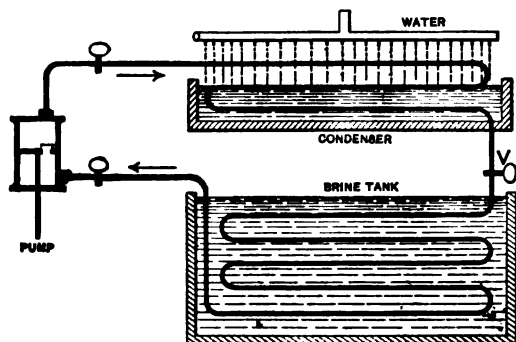
FIG. 62.—AMMONIA ICE-PLANT.
V, Expansion-valve.

The ammonia ice apparatus is shown in Fig. 52. Ammonia gas is pumped under great pressure into the condenser pipes, which are cooled by a shower of cold water. The liquefied ammonia is admitted through the expansion-valve *V* to the coils in the brine tank. The cold produced by the volatilization and expansion of the ammonia lowers the temperature of the brine to about − 20°. The water to be frozen is placed in prismatic vessels and lowered into the brine.

Tests.—Ammonia is recognized by its odor, by its alkalinity, and by the white fumes it gives with chlorin or hydrochloric acid. It is set free from its compounds by caustic alkalis. Its presence in small quantities is indicated by the Nessler test (page 212).

Nitrids.—The nitrids may be regarded as derivatives of ammonia, or as simple binary compounds of nitrogen with the metals. They are usually obtained by the action of metallic oxids or chlorids upon ammonia. They are mostly decomposed by heat, sometimes with explosion. They will be described in connection with the metals.

<div align="center">AMMONIUM (NH₄)′.</div>

Ammonia unites directly to acids to form salts:

$$NH_3 + HCl = NH_4Cl; \quad 2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

When it acts with the halogens it yields nitrogen and the ammonium halid:

$$4NH_3 + 3Cl = 3NH_4Cl + N.$$
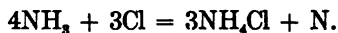
Its solution in water acts as if it contained a hydroxid, and the action may be expressed thus: $NH_3 + H_2O = NH_4OH$. Furthermore, ammonium hydroxid acts like other hydroxids:

$$KOH + HCl = KCl + H_2O; \quad NH_4OH + HCl = NH_4Cl + H_2O.$$

The simplest explanation of all these facts is in the hypothesis of the existence of a positive univalent radical $(NH_4)′$, which has been named *ammonium*. In ammonia the nitrogen is trivalent, while in the ammonium compounds its valence is five. While ammonia is saturated and yields derivatives by the replacement of its hydrogen, it still acts like an unsaturated compound because the valence of nitrogen so easily changes from three to five.

The ammonium radical has not been isolated. In its chemical properties it is closely allied to the alkali metals. Its salts generally are isomorphous with the potassium salts. Could it be obtained, it would probably be a light liquid or a gas. Its solutions contain the univalent positive ion (NH·₄).

<div align="center">AMMONIUM COMPOUNDS.</div>

The radical NH₄ enters into a very large number of compounds. It unites directly to the negative elements and replaces the hydrogen of acids. Its hydrogen atoms are replaceable and thus arise numerous derivatives chiefly organic. The chief commercial source of ammonium compounds is the ammoniacal liquor of the gas-works. This liquid is distilled with lime and the liberated

ammonia is conducted into water (ammonium hydroxid), or hydro-
chloric acid (ammonium chlorid), or sulfuric acid (ammonium sul-
fate).

All ammonium compounds are decomposed by heat.   In some
cases the molecule is completely broken up, while in others there
is a simple separation into ammonia and an acid.   They all yield
ammonia when heated with alkalis.   They are all soluble in water
except the double salts of certain metals, as, for example, am-
monium chloroplatinate $(NH_4)_2PtCl_6$.   Ammonium salts in solu-
tion are highly dissociated.   The heat of formation of the ion
$NH_4\cdot$ from the elements is 32,500 cal.

Only the principal ammonium compounds of the elements
already studied are given here.   The others will be treated in con-
nection with the remaining elements.

AMMONIUM HALIDS.

The ammonium halids are very similar to the alkali halids.
They are formed by the union of ammonia and the haloid acids.
They volatilize with dissociation, but the parts reunite when cooled.
They are all white, crystalline salts which dissolve in water with
the absorption of heat.   The thermal equations are as follows:

$(NH_3,HF) = 30,109$ cal.

$(NH_3,HCl) = 41,900$ c.	$(NH_4Cl,Aq.) = -3,900$ c.	$(N,H_4,Cl) = 75,800$ c.
$(NH_3,HBr) = 45,020$ c.	$(NH_4Br,Aq.) = -4,380$ c.	$(N,H_4,Br) = 65,348$ c.
$(NH_3,HI) = 43,462$ c.	$(NH_4I,Aq.) = -3,550$ c.	$(N,H_4,I) = 49,313$ c.

Ammonium Fluorid, NH_4F, is prepared by direct union of NH_3 and
HF, or by heating together in a covered platinum crucible potassium
fluorid and ammonium chlorid.   If the lid be kept cool, the NH_4F crys-
tallizes on the under surface.   It forms hexagonal prisms, has a sharp,
salty taste, and deliquesces in moist air.   Its solution in water slowly
decomposes.   It acts upon silicates, forming SiF_4, and hence etches glass.

Ammonium Chlorid, NH_4Cl.—This compound occurs native as
the mineral *sal ammoniac,* chiefly in the vicinity of volcanoes.   It
is usually prepared from the ammoniacal liquor of gas-works by
heating with lime and absorbing the evolved ammonia in hydro-
chloric acid.   It may also be obtained by heating a mixture of
sodium chlorid and ammonium sulfate.   It is purified by sublima-
tion.

Ammonium chlorid is a white solid with a sharp, saline taste and specific gravity 1.52. It crystallizes in regular octahedrons and fibrous masses. It dissolves in water at 0° 28.4 parts; at 10° 32.8 parts; and at 100° 77.2 parts. The saturated solution boils at 115°. It dissolves with absorption of heat. The solution is ionized, twentieth-normal 6 per cent, hundredth-normal 13 per cent, and is slightly acid by hydrolysis: $NH_4\cdot,Cl' + H_2O = NH_4OH + H\cdot,Cl'$. It sublimes when heated and dissociates at 350° into NH_3 and HCl.

Ammonium chlorid is the most important of the ammonium compounds except the hydroxid. It is used in medicine and in the arts, in soldering, tinning, dyeing, and in the preparation of ammonia, and as a common laboratory reagent.

Ammonium Bromid, NH_4Br, is a white crystalline solid obtained by union of NH_3 and HBr, or by the action of bromin on ammonium hydroxid.

Ammonium Iodid, NH_4I, is a colorless solid of specific gravity 2.5.

COMPOUNDS OF AMMONIUM WITH THE ELEMENTS OF GROUP VI B.

Ammonium Hydroxid, NH_4OH.—When ammonia dissolves in water the hydroxid is supposed to be formed, though it cannot be isolated. It is unstable, decomposing readily into NH_3 and H_2O. It has therefore the properties of ammonia gas. The solution contains the ions $NH_4\cdot$ and HO', decinormal 1.5 per cent.

Ammonium Hydrosulfid, NH_4SH, is obtained as a white, volatile, very soluble solid by saturating with H_2S an alcoholic solution of ammonia, or by bringing together equal volumes of dry NH_3 and dry H_2S at − 15°. It is obtained in solution by saturating aqueous ammonia with H_2S.

Ammonium Sulfid, $(NH_4)_2S$, is a white crystalline solid obtained by mixing one volume of H_2S with two volumes of NH_3 at − 18°. It dissociates at ordinary temperatures into NH_4SH and NH_3. Its aqueous solution is obtained by saturating ammonium hydrosulfid with ammonia, or by saturating a given volume of ammonia solution with H_2S, then adding an equal volume of ammonia solution of the same strength. Both this solution and the last turn yellow if exposed for some time to the air, because of the formation of polysulfids along with thiosulfates. This is called *yellow ammonium sulfid* and may be had at once by adding sulfur to NH_4SH solution.

Ammonium sulfid in its various forms is much used in the

laboratory as a reagent in analytic chemistry. It precipitates most of the metals as sulfids.

Polysulfids of Ammonium.—*Ammonium tetrasulfid*, $(NH_4)_2S_4$, sulfur-yellow crystals; *ammonium pentasulfid*, $(NH_4)_2S_5$, orange-yellow crystals; and *ammonium heptasulfid*, $(NH_4)_2S_7$, ruby-red crystals, are unstable compounds which slowly docompose, leaving a residue of sulfur.

Ammonium Hydroselenid, NH_4SeH, and **Ammonium Selenid**, $(NH_4)_2Se$, are both formed by the direct union of NH_3 and H_2Se, the first when H_2Se is in excess and the second when NH_3 is in excess. They are white solids which turn red on exposure to the air and dissociate when heated.

Ammonium Hydrotellurid, NH_4TeH, is formed by the union of equal volumes of NH_3 and H_2Te. It is a white, soluble, crystalline solid which volatilizes with dissociation at 80°.

Ammonium Salts.—Ammonium salts are very numerous, since the radical NH_4 acts like the alkali metals to replace the hydrogen of acids. They are generally white, crystalline solids, quite soluble in water and dissociate when heated.

Ammonium Chlorate, NH_4ClO_3, is obtained by saturating chloric acid with ammonia. It crystallizes in needles and has an acid taste.

Ammonium Perchlorate, NH_4ClO_4, is obtained as white, rhombic crystals by saturating ammonia with perchloric acid.

Ammonium Iodate, NH_4IO_3, lustrous plates of specific gravity 2.6, formed by the action of ammonia on iodic acid.

Ammonium Sulfites.—The normal *ammonium sulfite*, $(NH_4)_2SO_3$, and the acid salt, NH_4HSO_3, are white crystalline solids soluble in water and unstable. There are also double salts, such as $AgNH_4SO_3$.

Ammonium Sulfates.—Normal ammonium sulfate, $(NH_4)_2SO_4$, is prepared by neutralizing sulfuric acid with ammonia and evaporating. It forms rhombic crystals isomorphous with potassium sulfate. It has a specific gravity 1.76, melts at 140°, and decomposes above 280°. One hundred parts of water dissolve 71 parts at 0° and 97 parts at 100°. It is prepared in large quantities from the ammoniacal liquors of the gas-works and is used in the manufacture of other ammonium compounds. Its heat of formation is 282,200 calories, and its heat of solution is − 2600 calories.

The acid salt, NH_4HSO_4, is obtained by treating the normal salt with hot sulfuric acid. It forms rhombic prisms of specific gravity 1.79.

There are several other ammonium sulfates, among which are *ammonium disulfate*, $(NH_4)_2S_2O_7$, and *ammonium persulfate* $(NH_4)_2S_2O_8$.

Selenites, selenates, tellurites, and tellurates of ammonia have formulas and properties simular to those of the corresponding sulfur compounds.

Ammonium Chromates.—*Ammonium chromate*, $(NH_4)_2CrO_4$, as soluble, lemon-yellow needles, is obtained by evaporating a solution of CrO_3 in ammonia. *Ammonium dichromate*, $(NH_4)_2Cr_2O_7$, orange-colored monoclinic crystals, is also formed by the action of the trioxid upon ammonia. *Ammonium trichromate*, $(NH_4)_2Cr_3O_{10}$, and *ammonium hexachromate*, $(NH_4)_2Cr_6O_{19}$, are described. There are also several series of complex chromium ammonium salts, of which *chlorochromtetrammonium chlorid*, $Cl_2Cr_2N_4H_8(NH_4)_4Cl_4,2H_2O$, may be taken as an example.

Ammonium Molybdates.—Besides the normal *ammonium molybdate*, $(NH_4)_2MoO_4$, there are di, tri, tetra, and hepta molybdates, and a number of double salts in which ammonium is associated with some other element or radical. The ammonium molybdate of commerce is a *hexabasic heptamolybdate*, $(NH_4)_6Mo_7O_{24},4H_2O$.

Ammonium Tungstates.—The ammonium tungstates closely resemble the molybdates. The normal salt has not been prepared. The more common one is the *hexabasic heptatungstate*, $(NH_4)_6W_7O_{24},6H_2O$. Numerous other ammonium polytungstates, single and double, have been prepared.

Ammonium Uranates.—Several uranates, peruranates, and uranyl-uranates have been described.

AMIDOGEN $(NH_2)'$.

The hydrogen atoms of ammonia may be replaced by positive or negative elements or radicals. Thus are obtained two series of compounds called *amins* and *amids*. If one H is replaced, the compound is said to be *primary;* if two, *secondary;* and if three, *tertiary.* We have then the following forms, in which $\overset{+}{R}$ represents a positive, and $\overline{R}$ a negative element of radical: .

	Primary.	Secondary.	Tertiary.
Amins,	$\overset{\cdot}{R}NH_2$	$\overset{+}{R_2}NH$	$\overset{+}{R_3}N.$
Amids,	$\overline{R}NH_2$	$\overline{R_2}NH$	$\overline{R_3}N.$

In the secondary and tertiary forms we may have at the same time positive and negative replacing elements, forming compounds similar to ternary salts. These are called *alkalamids*.

These combinations seldom occur outside of organic compounds. By taking an H from ammonia there remains the univalent radical

NH₂, which is called *amidogen,* and is a constituent of thousands of organic compounds.

Hydroxylamin, NH₂OH.—This compound was discovered by Lossen in 1865. It may be regarded as a union of hydroxyl and amidogen, or as ammonia in which an H has been replaced by hydroxyl. It is prepared by reducing nitrogen dioxid, nitric acid, or certain nitrates with nascent hydrogen:

$$N_2O_2 + 3H_2 = 2NH_2OH.$$
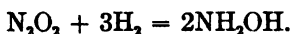
The preparation may be conducted as follows : Granulated tin and dilute hydrochloric acid with a few drops of platinic chlorid are placed in a flask and N₂O₂ made to bubble through the mixture. Hydroxylamin hydrochlorid passes into solution. The tin is precipitated with H₂S and the liquid filtered and evaporated to dryness. The residue is treated with absolute alcohol, which dissolves the hydroxylamin hydrochlorid. The alcohol is evaporated and sulfuric acid added, which forms hydroxylamin sulfate. Barium hydroxid is now added and the barium sulfate filtered off. The filtrate is a solution of hydroxylamin.

Hydroxylamin is a crystalline solid which melts at 33° and boils at 57°. It is unstable, decomposing with violence when heated, yielding NH₃, H₂O, and N. It is feebly basic and slightly ionized. It unites directly to acids, the N becoming pentavalent:

NH₂OH + HCl = NH₂OHHCl, Hydroxylamine hydrochlorid.
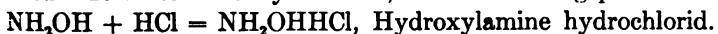
It has a strong reducing action, precipitates gold and mercury from solution, and reduces cupric to cuprous salts. Its salts are decomposed by heat, some of them with violence. Its heat of formation is 24,400 cal.

HYDRAZIN, N₂H₄.

Hydrazin is free amidogen, two radicals uniting to form a saturated compound, H₂N − NH₂. It was first prepared by Curtius in 1887. It may be obtained by heating its hydroxid with barium monoxid in a closed tube to 170°:

$$(NH_2)_2H_2O + BaO = Ba(HO)_2 + (NH_2)_2.$$

It is a colorless, poisonous gas with a peculiar odor. It is the strongest reducing agent known. It boils at 114° and solidifies at 1°. It unites directly to acids to form salts:

N₂H₄ + HCl = (N₂H₄)HCl, or H₂N − NH₃Cl, Hydrazin hydrochlorid.
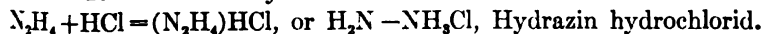
Hydrazin Hydroxid or **Hydrate,** $N_2H_4H_2O$.—Hydrazin unites vigorously to water to form the hydroxid which dissolves in all proportions, forming an alkaline solution. The hydroxid decomposes when boiled, but a portion goes over with the steam unchanged. It has a reducing action like hydroxylamin, and forms salts with the acids, as N_2H_4HCl and $N_2H_4H_2SO_4$.

HYDRAZOIC ACID (AZOIMID).

Hydrazoic acid, $\begin{smallmatrix} N \\ \| \\ N \end{smallmatrix}\!\!\!\searrow N - H$, was discovered by Curtius in 1890. It is obtained by the reduction of various organic hydrazin compounds. The theoretical reaction may be illustrated as follows :

$$H_2N - NH_2Cl + NaNO_2 = \begin{smallmatrix} N \\ \| \\ N \end{smallmatrix}\!\!\!\searrow N - H + 2H_2O + NaCl.$$
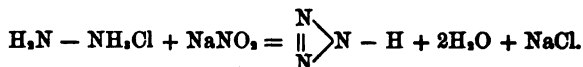
It is also obtained by the action of sodamin upon hyponitrous oxid:

$$2NaNH_2 + N_2O = NH_3 + NaHO + NaN_3.$$

This sodium salt is distilled with sulfuric acid.

Hydrazoic acid is a colorless, very poisonous gas, producing when breathed dizziness, headache, and inflammation of the mucous membrane. It fumes with ammonia, forming *ammonium hydrazoate,* NH_4N_3. It dissolves in water to an acid solution which is slightly dissociated into the ions $H\cdot$ and N_3'. It boils at 37° and explodes with violence. With silver nitrate it gives *silver hydrazoate,* $Ag'N_3$. It dissolves in water in all proportions and the solution acts like the gas.

COMPOUNDS OF NITROGEN WITH THE HALOGENS.

Nitrogen forms compounds with chlorin, bromin, and iodin, all of which are endothermic, unstable, and violently explosive. They are obtained from ammonia or its derivatives by replacement, and hence may have either of the three forms, NH_2I, NHI_2, or NI_3. Their composition is not very definitely known, and it is possible that mixtures of two or more derivatives sometimes occur.

Nitrogen Chlorid, NCl_3.—This dangerously explosive compound was discovered by Dulong in 1811. In experimenting with it he lost an eye and three fingers. In 1813 Faraday and Davy both suffered injuries from the explosion of small quantites of it.

It is produced by the action of chlorin in excess upon ammonium chlorid:

$$NH_4Cl + 3Cl_2 = 4HCl + NCl_3.$$
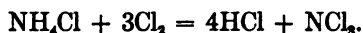
Illustrations.—A flask filled with chlorin is dipped mouth down into a solution of ammonium chlorid warmed to 80°. As the chlorin is absorbed, drops of NCl_3 form at the surface of the water, sink, and are caught in a leaden saucer placed beneath the mouth of the flask. As soon as a few drops have collected the saucer is removed with clean tongs and another put in its place. The chlorid is exploded by touching it with a feather dipped in turpentine and attached to a long stick.

Its formation may also be shown by the electrolysis of a saturated solution of ammonium chlorid whose surface is covered with a thin layer of oil of turpentine. The NCl_3 separates at the positive pole in small drops, which, rising, explode on coming in contact with the turpentine.

Nitrogen chlorid is a thin, yellow, oily liquid of specific gravity 1.65. It is volatile, has a pungent odor, and the vapor attacks the eyes. It is dangerously and violently explosive. On contact with oils, phosphorus, or turpentine it decomposes with a loud noise. It is decomposed by hydrochloric acid and ammonia, the first reaction being the exact reverse of the one by which it is prepared and the second showing why it is not formed in the presence of an excess of ammonia. Its heat of formation is − 38,100 calories.

Nitrogen Bromid, NBr_3, is formed when potassium bromid is added to nitrogen chlorid under water. It is a dark-red explosive liquid.

Nitrogen Iodid, NI_3 or NHI_2.—By the action of ammonia upon iodin either solid or in solution in alcohol, or in aqueous potassium iodid, a highly explosive black compound is formed whose constitution is not definitely known and which seems to depend upon the method of its preparation. Three formulas have been given: NI_3, NHI_2, and $N_2H_3I_3$ (or NI_3, NH_3).

The formation and instability of this substance may be shown as follows: To a few crystals of iodin in a small dish add strong ammonia solution and stir for a few minutes. Wash away the greater part of the ammonia, pour off the wash water, and separate the black powder into small lumps on pieces of filter-paper. When these are dry, they explode at the slightest touch and often spontaneously.

OXIDS OF NITROGEN.

The oxids of nitrogen are unstable, loose compounds in which the valence of nitrogen seems to be I, II, III, IV, or V. It is proba-

ble, however, that two of these compounds are radicals and that the real valences of nitrogen are as the theory requires, I, III, and V. The formulas and names are as follows:

Hyponitrous oxid (Nitrous oxid), N_2O N—O—N

Nitrogen dioxid (Nitric oxid), N_2O_2 O=N—N=O

Nitrous oxid (Nitrogen trioxid), N_2O_3 O=N—O—N=O

Nitrogen tetroxid (peroxid), N_2O_4 $\mathrm{O{\searrow}N{-}N{\nearrow}O}$ with O below

Nitric oxid (Nitrogen pentoxid), N_2O_5 $\mathrm{O{\searrow}N{-}O{-}N{\nearrow}O}$ with O

HYPONITROUS OXID (NITROUS OXID).

Formula N_2O. Molecular weight 44. Density 22. Liter weighs 1.97 grams.

History.—Hyponitrous oxid was first prepared by Priestley in 1772, and was liquefied by Faraday in 1823.

Preparation.—Hyponitrous oxid is produced in the reduction of nitrogen dioxid or nitric acid by metals, sulfites, sulfids, and other easily oxidizable substances. It is most conveniently prepared by gently heating ammonium nitrate:

$$NH_4NO_3 = 2H_2O + N_2O.$$

The gas is collected over warm water, brine, or mercury, or by displacement. When it is to be inhaled, it should be passed through ferrous sulfate solution to remove other oxids of nitrogen which may have been formed, and through potassium-hydroxid solution to absorb any chlorin which may have come from ammonium chlorid occurring as an impurity in the ammonium nitrate.

Physical Properties.—Hyponitrous oxid is a colorless gas with a rather pleasant odor and a sweetish taste, and with specific gravity 1.52 (air = 1). One volume of water dissolves 1.3 volumes at 0°; 0.9 volume at 10°; and 0.6 volume at 25°. Alcohol dissolves about three times as much. At 0° and 30 atmospheres it becomes a colorless, mobile liquid of specific gravity 0.937 which boils at − 92°, and it freezes to a solid which melts at − 99°. A mixture of the liquid with carbon disulfid evaporating *in vacuo* lowers the temperature to − 140°. In contact with the skin it produces blisters.

Chemical Properties.—Hyponitrous oxid is a vigorous supporter of combustion. Ignited wood, phosphorus, iron, sulfur, potassium,

and sodium burn brightly in it.   Mixed with hydrogen it is explosive, and when the two gases combine in a eudiometer the residual nitrogen equals in volume the N_2O used:

$$N_2O + H_2 = N_2 + H_2O.$$

Its heat of formation is $-$ 18,000 calories.

Physiological Properties.—When breathed hyponitrous oxid produces a nervous excitement which often causes boisterous laughter; whence the name *laughing-gas.* If the inhalation be continued, insensibility follows and finally death. If air be breathed again even after insensibility has set in, the effects soon pass away.   The gas was formerly much used as an anesthetic in minor surgical operations and especially in dentistry.

Tests.—Hyponitrous oxid is distinguished from oxygen, which it much resembles in properties, by the fact that it does not produce red vapors with nitrogen dioxid.

<div align="center">NITROGEN DIOXID (NITRIC OXID, NITROSYL).</div>

<div align="center">Formula N_2O_2 or NO.   Molecular weight 60 or 30.   Density 80 or 15.</div>

History.—Nitrogen dioxid was discovered by Van Helmont and further investigated by Priestley.

Preparation.—Nitrogen dioxid is formed by the decomposition and reduction of nitric acid and nitrates in various ways:

1. By the action of metals on dilute nitric acid, the nitrate of the metal being formed and the nascent hydrogen liberated acting upon another portion of the acid to reduce it :

$$Cu + 2HNO_3 = Cu(NO_3)_2 + H_2;   3H + HNO_3 = 2H_2O + NO,$$

or $$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$
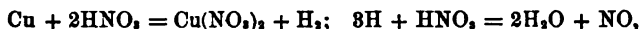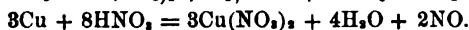
The acid should be dilute, since the strong acid sets free nitrogen and its higher oxids.

2. By the action of ferrous sulfate upon nitric acid or nitrates in the presence of sulfuric acid:

$$6FeSO_4 + 2KNO_3 + 5H_2SO_4 = 2HKSO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

3. By the action of ferrous chlorid upon nitrates in the presence of hydrochloric acid :

$$3FeCl_2 + KNO_3 + 4HCl = 3FeCl_3 + KCl + 2H_2O + NO.$$

The preparation of nitrogen dioxid may be conducted in a flask furnished with a separatory funnel or funnel-tube and delivery-tube as follows:

1. Place in the flask copper strips and add dilute nitric acid (sp. gr. 1.2) in portions through the funnel-tube; or,

2. Place in the flask a mixture of one part sodium or potassium nitrate and four parts ferrous sulfate, or strips of copper covered with a saturated solution of potassium nitrate, and add sulfuric acid drop by drop through the funnel.

The gas is collected over water, which dissolves the higher oxids that are generally formed.

Physical Properties.—Nitrogen dioxid is a colorless gas of specific gravity 1.038. Its odor and taste cannot be ascertained, as it combines at once with the oxygen of the air. It is but slightly soluble in water, but dissolves readily in solutions of ferrous salts, turning them brown, and is expelled again by heat. It is quite soluble in nitric acid, forming a brown or greenish solution which is supposed to contain N_2O_3. It is liquefied at $-154°$ and its critical temperature and pressure are $-93°$ and 71 atmospheres. The vapor density of the gas is 15, corresponding to the formula NO. Nitrogen therefore appears to be divalent, but it is more probable that NO is a univalent radical, N_2O_2 being dissociated at the temperature of the density determination.

Chemical Properties.—Nitrogen dioxid is the most stable of the oxids of nitrogen. It will sustain a dull red heat without decomposition. It is not a ready supporter of combustion, though substances well ignited will burn in it. Phosphorus burns, while sulfur is extinguished. Carbon disulfid burns in the gas with a bluish-white, highly actinic flame. It unites directly to the oxygen of the air to form brown N_2O_4 or N_2O_3, and to chlorin and bromin to form the oxychlorid and oxybromid. It is strongly endothermic, the heat of formation being $-21,500$ calories.

Illustrations.—The union of nitrogen dioxid with oxygen to form the brown oxids may be shown by emptying a jar of the gas in the air.

To show its action with carbon disulfid add a small quantity of this substance (2 cc. to the liter) to a jar of the gas, invert a few times to insure the mixture, then remove the cover and ignite.

NITROUS OXID (NITROGEN TRIOXID).

Formula N_2O_3.   Molecular weight 76.   Density 88.

Preparation.—Nitrous oxid is formed:

1. By direct union of four volumes of NO with one volume of oxygen at 18°: $4NO + O_2 = 2N_2O_3$.

2. By union of N_2O_3 with liquid N_2O_4: $N_2O_4 + N_2O_2 = 2N_2O_3$.

3. By dissolving N_2O_3 in well-cooled anhydrous nitric acid:

$$2HNO_3 + 2N_2O_3 = 3N_2O_3 + H_2O.$$
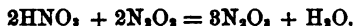
4. By acting upon nitric acid with arsenous oxid or other reducing agents and cooling the evolved gases. The brown gas obtained by this reaction at the ordinary temperature is a mixture of NO and NO_2 in varying proportions.

Properties.—Nitrous oxid only exists at low temperatures. Above 0° it dissociates into NO and NO_2. At $-20°$ it is a dark-blue liquid of specific gravity 1.449. As the temperature rises it begins at once to decompose and boils freely at 4°. Its chemical properties are those of the two gases into which it dissociates.

NITROGEN TETROXID (NITROGEN DIOXID, NITROGEN PEROXID,
NITRYL).

Formula NO_2 or N_2O_4. Molecular weight 92 or 46. Density 46 or 23.

Preparation.—Nitrogen tetroxid is formed:

1. By union of nitrogen dioxid with oxygen : $N_2O_2 + O_2 = N_2O_4$.

2. By heating dry lead nitrate : $Pb(NO_3)_2 = PbO + N_2O_4 + O$.

3. By the action of arsenous oxid upon warm nitric acid. In this action there are produced several oxids which are converted into N_2O_4 by the addition of oxygen.

The gas is condensed in a U-tube immersed in a freezing mixture.

Properties.—Nitrogen tetroxid is a colorless liquid without a very definite boiling- or freezing-point. When strongly cooled it becomes a crystalline solid which melts at $-12°$. Dissociation begins at 0° and the liquid turns brown because of dissolved NO_2, the color deepening as the temperature rises. At about 22° it boils, giving a brown vapor which contains 20 per cent of NO_2. At 140° the dissociation is complete. As NO_2 it is a brown gas.

Nitrogen tetroxid is decomposed by water with formation of nitric and nitrous acids, while NO_2 yields nitric acid and NO. It is a poor supporter of combustion. As a gas it is suffocating and poisonous, producing headache and dizziness. It forms peculiar compounds with certain metals, as Cu_2NO_2, Co_2NO_2, Ni_2NO_2, and Fe_2NO_2, called copper nitroxyl, etc.

Illustration.—To show the union of N_2O_2 with oxygen and the solution of N_2O_4 in water, fill a long tube inverted over water with N_2O_2 and introduce gradually oxygen from a bag or gas-holder. As fast as the N_2O_4 is

formed, it dissolves and the water rises in the tube. By taking care not to use too much oxygen the water can be made to fill the tube entirely.

NITRIC OXID (NITROGEN PENTOXID).

Formula N_2O_5. Molecular weight 108. Density 54.

Preparation.—Nitric oxid was discovered by Deville in 1842. It is prepared by passing dry chlorin or nitrosyl chlorid over dry silver nitrate:

$$AgNO_3 + NOCl = AgCl + N_2O_5;$$
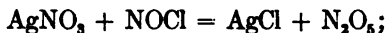
or by reduction of nitric acid with phosphorus pentoxid:

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5.$$
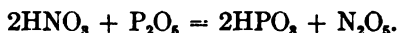
To prepare the oxid by the last method, add strong nitric acid in proper quantity to P_2O_5 in a well-cooled retort and distil with a gentle heat, condensing the nitric oxid in a cooled receiver. No cork nor rubber must be used in the connections.

Properties.—Nitric oxid is a white solid which crystallizes in rhombic prisms, melts at 30°, and boils with decomposition at about 47°. It explodes when warmed, and at the ordinary temperature gradually separates into N_2O_4 and O. It unites vigorously to water, forming nitric acid and evolving much heat:

$$N_2O_5 + H_2O = 2HNO_3 + 29,800 \text{ cal.}$$

OXYHALIDS OF NITROGEN.

The univalent radicals NO and NO_2 enter into many compounds, mostly organic, which are called *nitroso* and *nitro* compounds respectively. They may be regarded as compounds of the radicals, or as obtained by replacing the hydroxyl of nitrous and nitric acids.

Nitrosyl Chlorid, NOCl, may be formed:

1. By direct union, as $NO + Cl = NOCl$.

2. By action of phosphorous pentachlorid upon nitrites:

$$PCl_5 + KNO_2 = KCl + POCl_3 + NOCl.$$

3. By heating aqua regia: $HNO_3 + 3HCl = 2H_2O + Cl_2 + NOCl$.

Nitrosyl chlorid is an orange-yellow gas condensing to a liquid which boils at $-56°$ and freezes at $-60°$. Its critical temperature is $-163°$. It is decomposed by water and metallic oxids and hydroxids.

Nitrosyl Bromid, NOBr, is formed by direct union when NO is conducted into bromin at $-10°$. It is a dark-brown liquid which begins to decompose at 2° and at 20° leaves a red liquid which has the decomposition $NOBr_3$.

ACIDS OF NITROGEN.

The acids of nitrogen correspond to the regular oxids and are as follows:

Hyponitrous acid (ortho),   HNO   H—O—N

Nitrous acid (monometa),   HNO$_2$ H—O—N$=$O

Nitric acid (dimeta),   HNO$_3$ H—O—N$\big\langle{}^{O}_{O}$

These acids follow the rule of taking the lowest meta form and are all monobasic. The hydrated acids have not been separated nor are their salts known. The acid ions of nitrogen are $\overline{NO}'$, $\overline{NO_2}'$, and $\overline{NO_3}'$.

HYPONITROUS ACID.

Formula HNO.   Molecular weight 31.   Density 15.5.

Preparation and Properties.—Hyponitrous acid is only known in solution and cannot be obtained by direct hydration of hyponitrous oxid, to which it corresponds. It is formed when silver hyponitrite is decomposed with hydrochloric acid, $AgNO + HCl = AgCl + HNO$. The solution is colorless, acid, and somewhat stable. It liberates iodin from potassium iodid and reduces permanganate solution.

Hyponitrites are obtained by reduction of nitrates and nitrites by means of the nascent hydrogen set free from water by sodium.

NITROUS ACID.

Formula HNO$_2$.   Molecular weight 47.   Density 28.5.

Preparation.—Nitrous acid has not been obtained free. It is formed by direct union of nitrous oxid and water, $N_2O_3 + H_2O = 2HNO_2$, but is so unstable that it soon decomposes into nitric acid, water, and nitrogen dioxid: $3HNO_2 = HNO_3 + N_2O_3 + H_2O$. It is both a reducing and an oxidizing agent. Its heat of formation is $(H,N,O_2,Aq.) = 30,770$ cal.

Nitrites.—Nitrites are quite stable and occur in small quantities widely distributed in nature. They are formed in the soil in the oxidation of nitrogenous organic matters, but are soon themselves oxidized to nitrates. They are decomposed by dilute acids with liberation of nitrous acid, which decolorizes potassium permanganate solution and blues KI starch solution. These actions constitute delicate tests for nitrites.

Ammonium Nitrite, NH_4NO_2, is obtained by adding ammonium chlorid to silver-nitrite solution. It is a white crystalline deliquescent solid. It is found in small quantities in the air and in terrestrial waters.

NITRIC ACID.

Formula HNO_s. Molecular weight 63. Density 81.5. Specific gravity 1.54.

Occurrence.—Free nitric acid does not occur in nature unless it be momentarily when it is liberated by some chemical process. Its salts, the nitrates, however, are abundant and widely distributed. The principal ones are the nitrates of potassium, sodium, calcium, and ammonium.

History.—Nitric acid was known to the alchemists under the name of *aqua fortis* and was used in the separation of gold from silver. In 1776 Lavoisier proved that it contained oxygen, and in 1784 its true composition was determined by Cavendish.

Preparation.—Nitric acid is prepared:

1. By dissolving nitric oxid or nitrogen tetroxid in water:

$$N_2O_4 + H_2O = 2HNO_3.$$

2. By distilling nitrates with sulfuric acid:

$$2KNO_3 + H_2SO_4 = K_2SO_4 + 2HNO_3.$$
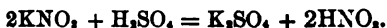
To prepare nitric acid in the laboratory heat in a retort equal parts of niter and sulfuric acid. The nitric acid distils over and is condensed in a cooled receiver. The acid thus prepared is brown because of dissolved NO_2, and also contains some water. To get rid of these, redistil with an equal volume of sulfuric acid and pass through the warm distillate a current of dry air. In this way an acid is obtained which contains less than one half of one per cent of water.

The commercial acid is prepared by distilling sodium nitrate and sulfuric acid in iron cylinders partly lined with fire-clay; or by oxidizing the nitrogen of the air by means of electric arcs of high voltage.

Physical Properties.—Nitric acid is a colorless fuming liquid of specific gravity 1.55 at 0°. At 47° it becomes a crystalline solid. It begins to boil at 86°, partially decomposing into water, oxids of nitrogen, and oxygen. The temperature rises to 120.5°, at which point it remains constant, giving a distillate which has a specific gravity 1.414 and contains 68 per cent of HNO_3. If the dilute acid be boiled, it gives off water until the same strength is reached.

When the strong acid is mixed with water the volume contracts and the temperature rises, the effect being greatest when one molecule of the acid is mixed with three of the water. The heat of solution is 7200 calories. The specific gravity of the acid of various

strengths at 15° is as follows: 100 per cent 1.53, 80 per cent 1.46, 60 per cent 1.37, 40 per cent 1.25, 20 per cent 1.12, 10 per cent 1.06.

Chemical Properties.—Nitric acid is unstable and chemically very active. It decomposes partially at the ordinary temperature and completely at 256°. Light assists the decomposition. It oxidizes sulfur, phosphorus, carbon, hydrogen, organic matters, and all the metals except gold and platinum. In its action upon metals no hydrogen is evolved because this is oxidized as fast as it is set free. Generally there is produced the nitrate of the metal or the acid of the non-metal, together with water and one or more of the oxids of nitrogen, and sometimes ammonia or hydroxylamin. With oxids it acts like other acids. Some typical reactions are as follows:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + N_2O_2.$$
$$5Zn + 13HNO_3 = 5Zn(NO_3)_2 + 5H_2O + NH_3 + N_2O_4.$$
$$I + 3HNO_3 = HIO_3 + H_2O + N_2O_3 + NO_2.$$
$$Na_2O + HNO_3 = 2NaNO_3 + H_2O.$$
$$Sn + HNO_3 + 2HCl = SnCl_2 + NO_2 + NH_2OH.$$
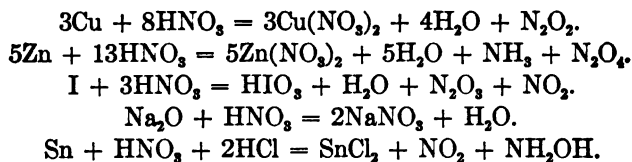
Nitric acid acts upon many organic compounds, replacing H with the NO_2 radical. Glycerin is thus converted into nitroglycerin:

$$C_3H_8O_3 + 3HNO_3 = 3H_2O + C_3H_5O_3(NO_2)_3.$$
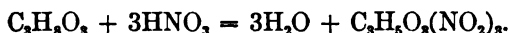
It destroys vegetable colors and turns organic substances yellow and decomposes them.

Nitric acid is more highly dissociated and therefore stronger than any other acid except hydrochloric. The percentage of dissociation is as follows: Normal solution 87, decinormal 94, centinormal 99.8, two-hundredth normal 100. The nitrate ion, NO_3', is colorless, unstable, and active. Its heat of formation is 49,700 cal.

Commercial nitric acid is yellow in color and contains various impurities: chlorin and iodic acid from the sodium nitrate; sulfuric acid, sodium sulfate, and iron oxid carried over mechanically in the distillation; and nitrogen dioxid resulting from the decomposition of the acid. These impurities may be mostly removed by distillation. The chlorin and nitrogen dioxid come off first and the distillate containing them is rejected. A small residue left in the vessel contains the other impurities.

Illustrations.—To show the oxidizing action of nitric acid add a little of it to some sawdust which has been heated almost to charring in a dish. The sawdust takes fire. Add a few drops of the acid to a solution of ferrous sulfate and boil ; it becomes ferric sulfate. Add a small bit of phosphorus to strong nitric acid ; it burns with violence.

To show its action upon metals place a strip of zinc or copper in the strong acid and note the evolution of heat and the red fumes of NO_2 and N_2O_3.

Physiological Properties.—Nitric acid is a corrosive poison, has a stifling odor, burns the skin and turns it yellow.

Tests.—Strong nitric acid is easily recognized by the red fumes which it gives when it acts upon metals. Nitrates are decomposed by sulfuric acid. Thus if to a solution of nitrates sulfuric acid be added and then the metal, the red fumes appear.

For small quantities and traces of nitric acid there are several delicate tests. The following is very convenient : Add to the solution to be tested a crystal of ferrous sulfate and pour down the side of the tube a little sulfuric acid. If nitrates are present, a brown ring will appear at the juncture of the two liquids.

Another test fluid is a one per cent solution of aniline in 15 per cent sulfuric acid. A few drops are added to a cc. of sulfuric acid in a porcelain dish and a drop of the liquid to be tested allowed to flow down the side of the dish. When the liquids meet a red color appears if nitrates are present, and the depth of the color indicates the quantity.

Brucine furnishes a still more delicate test. Add to a drop of the solution to be tested a drop of brucine solution and then a few drops of sulfuric acid. A pink color indicates nitrates. One part in 100,000 may be detected in this way.

Uses.—Nitric acid is much used in laboratories and in the arts. It is employed in the manufacture of aniline colors, nitroglycerin, guncotton, celluloid, sulfuric acid, numerous organic compounds, and the nitrates of silver, iron, lead, aluminum, barium, strontium, etc.

Fuming Nitric Acid.—Nitric acid which contains much NO_2 in solution is reddish yellow in color, has specific gravity 1.54, and is a more active oxidizer than the pure acid. It is called *fuming nitric acid*. It is easily obtained by distilling a mixture of four parts starch and 100 parts KNO_3 with 100 parts H_2SO_4. When diluted with water it becomes first green, then blue, and finally colorless. NO_2 is given off first, then NO. The colors are due to the formation of nitrous acid. The reactions are as follows:

$$2NO_2 + H_2O = HNO_3 + HNO_2; \quad 3HNO_2 = HNO_3 + H_2O + 2NO.$$
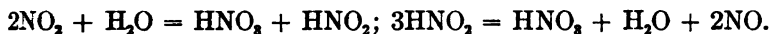
Aqua Regia.—A mixture of one part of nitric acid and three parts of hydrochloric acid dissolves gold and was for that reason called by the ancients *aqua regia.* The name is first mentioned by Basil Valentine (fifteenth century), but the acid was known to Geber in the sixth century. It is a powerful solvent and oxidizer, this action being due to chlorin and nitrosyl chlorid set free by the decomposition of the acids: $HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$.

Aqua regia has a reddish-yellow color and an irritating, acid, and chlorin-like odor. Its properties include those of its four constituents. It does not keep long, as the chlorin gradually reacts with water to form HCl. It is used for dissolving gold, platinum, certain ores, compounds not soluble in other acids, and as an oxidizing agent.

Illustration.—Place two cc. of nitric acid in one tube and six cc. of hydrochloric acid in another and add a fragment of gold leaf to each. The gold is not affected, but pour the liquids together and it soon dissolves.

Nitrates.—Nitric acid is monobasic and forms only normal salts. Nitrates are formed by dissolving metals or their oxids or carbonates in nitric acid more or less dilute. They are mostly soluble in water and crystallize well. Many are anhydrous, others have water of crystallization.   -

Nitrates melt readily and decompose at high temperatures, partially at first, forming nitrites, then completely. With sulfuric acid they give nitric acid. They are unstable and powerful oxidizers and form with combustibles detonating mixtures. They are formed in the soils by the oxidation of decaying nitrogenous organic matters in the presence of alkalies.

Chromic Nitrate, $Cr_2(NO_3)_6 + 18H_2O$, is obtained by dissolving Cr_2O_3 in nitric acid. The solution is blue by transmitted and red by reflected light. On evaporation a green solid is obtained which crystallizes in purple oblique prisms.

Uranyl Nitrate, $UO_2(NO_3)_2 + 6H_2O$, is obtained by dissolving any oxid of uranium in nitric acid. It forms yellow fluorescent rhombic prisms which deliquesce in moist air.

Ammonium Nitrate, NH_4NO_3, occurs in small quantities in air, soils, and waters. It is a white deliquescent crystalline solid with a bitter, salty taste and a specific gravity 1.7. It dissolves in water with lowering

of temperature. If 60 parts are dissolved in 100 parts of water at 18°, the temperature sinks to − 18°. The freezing-point of the saturated solution is − 17.7°. It melts at 159°, but begins to decompose at a much lower temperature (86°) into hyponitrous oxid and water. It may be prepared by neutralizing nitric acid with ammonia or ammonium carbonate. On evaporation it crystallizes in long striated prisms or in a fibrous mass.

Hydroxylamin Nitrate, NH_2OH,HNO_3, or $H_2N<^{O-H}_{O-NO_2}$, is formed by direct union of its constituents. It decomposes with explosive violence when heated.

NITROGEN WITH SULFUR AND SELENIUM.

Nitrogen Sulfid, N_2S_3, is obtained by the action of ammonia upon the chlorid or dichlorid of sulphur. It forms beautiful, yellow, rhombic crystals which sublime at 135°, melt with decomposition at 150°, and detonate on percussion. It has a faint odor, but irritates painfully the mucous membrane of the nose and eyes.

Nitrogen Selenid, N_2Se_2, is formed by the action of ammonium upon selenium tetrachlorid. It has properties similar to those of nitrogen sulfid.

MIXED COMPOUNDS OF NITROGEN AND SULFUR.

Several mixed compounds of nitrogen and sulfur have been formed whose constitution is not very well known. In most cases only the salts are known, the acid not having been separated. In this connection, however, the acid formulas are used:

Nitrosulfonic acid, $^{NO_2}_{HO}>SO_2$; Nitrosulfonic chlorid, $^{NO_2}_{Cl}>SO_2$;

Nitrosulfonic oxid, $(NO_2—SO_2)_2O$; Ammon-disulfonic acid, $NH_2(HSO_3)_2$.

The most important of these compounds is the nitrosulfonic acid, or as it is generally called, nitrosylsulfuric acid, which is, as we have seen, an intermediate product in the manufacture of sulfuric acid.

PHOSPHORUS.

Symbol P. Atomic weight 31. Density 62. Molecular weight 124.
Molecular formula P_4 or $\begin{matrix} P-P \\ \| \quad \| \\ P-P \end{matrix}$. Valence III and V. Melting-point 44.4°.

Occurrence.—Phosphorus does not occur free, but its native compounds are quite numerous. It is found in waters fresh and salt and in nearly all rocks and soils. It is an essential constituent

of bone, nervous and muscle tissue.   It is eliminated from the animal body through the kidneys as sodium ammonium phosphate, $NaNH_4HPO_4$. The principal minerals containing phosphorus are *phosphorite*, $Ca_3(PO_4)_2$; *apatite*, $3Ca_3(PO_4)_2,CaF_2$; *wavelite*, $2Al_2(PO_4)_2,Al_2(HO)_6,9H_2O$; and *vivianite*, $Fe_3(PO_4)_2,8H_2O$.

History.—Phosphorus was first obtained by the alchemist Brand of Hamburg (1669) by distilling a mixture of sand and evaporated urine.   Gahn in 1869 found that calcium phosphate was a constituent of bone, and in 1771 Scheele published a method of preparing phosphorus from bone-ash. Until 1772 phosphorus was considered a compound of phlogiston with an acid.   At that time Lavoisier showed that the product of its combustion in the air was heavier than the phosphorus burned, and in 1789 he proved that phosphoric acid contained phosphorus and oxygen.

The name phosphorus, which means *light-bearer*, was applied to any substance that was luminous in the dark.   To distinguish this substance from the others it was called *phosphorus mirabilis*, or Brand's, or Boyle's or English phosphorus.

Preparation.—Phosphorus is prepared by reduction of phosphates with carbon.   Bone-ash is mostly used, though much phosphorus is manufactured from native phosphates.   The process of preparation may be carried out as follows:

The bone-ash or native phosphate is first digested with sufficient sulfuric acid to convert the normal calcium phosphate into the acid salt:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$
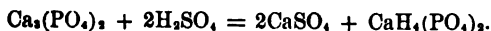
The acid phosphate remains in solution and is separated from the precipitated calcium sulfate by filtration.   It is then mixed with charcoal or sawdust, evaporated to dryness in leaden vessels, and raised to a dull-red heat, whereby water is driven off and calcium metaphosphate formed:

$$CaH_4(PO_4)_2 = 2H_2O + Ca(PO_3)_2.$$

The mixture is now transferred to bottle-shaped earthenware retorts so arranged in a furnace that the mouths project at the sides and are connected by vertical pipes with vessels of water.   These retorts are raised to a white heat when decomposition takes place, as follows:

$$3Ca(PO_3)_2 + 10C = Ca_3(PO_4)_2 + 10CO + 4P.$$

If the requisite amount of quartz sand be added the whole of the phosphorus may be liberated as follows:

$$2Ca(PO_3)_2 + 2SiO_2 + 10C = 2CaSiO_3 + 10CO + 4P.$$
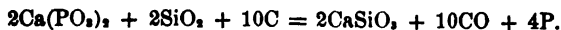
The phosphorus distils over, passes down through the vertical pipe into the cold water, where it solidifies, and the carbon monoxid bubbles through the water and escapes. The process is dangerous and difficult, because of the inflammability and poisonous nature of phosphorus.

The crude phosphorus thus obtained contains impurities mechanically carried over, and is dark in color. Various methods of purification are used. It may be pressed through chamois skin, or redistilled, or treated with a mixture of sulfuric acid and potassium dichromate.

The purified phosphorus is melted in a vessel surrounded with hot water and drawn off at the bottom into a horizontal tube surrounded with cold water. The stick of phosphorus is drawn out as fast as it cools and broken into pieces of equal lengths. The usual size is one half inch in diameter and seven inches long.

Most of the world's supply of phosphorus, about 3000 tons, is made in three factories, one at Oldbury, England, one at Lyons, France, and one at Niagara Falls. At the last place an electric process is used.

Physical Properties.—Phosphorus exists in two allotropic modifications, called *yellow phosphorus* and *red phosphorus*.

Yellow phosphorus is a translucent, wax-like solid of specific gravity 1.82 at 16°. At 0° it is brittle and crystalline. It is luminous in the dark and has an odor resembling that of garlic. It is always kept under water because it oxidizes so readily in the air. It soon loses its transparency and becomes coated with a white film, and when exposed to light gradually turns red. It melts under water at 44.4° and in a closed vessel without water at 30°, giving a yellow liquid which has a specific gravity 1.76. When cooled this liquid does not solidify until considerably below its melting-point, but when touched with a bit of solid phosphorus it congeals at once. It boils at 269°, giving a colorless vapor which has a density 62, indicating a molecular weight 124 and a molecular formula P_4. It sublimes *in vacuo* at a temperature below its melting-point, and crystallizes in rhombic dodecahedrons. Large crystals may be obtained by sealing phosphorus in a vessel filled with carbon dioxid and keeping it in the dark for several days with the bottom of the vessel warmed to 40°. It is insoluble in water, slightly soluble in alcohol, chloroform, benzene, and ether, very soluble in carbon disulfid (one part dissolves 9.26 parts P). Crystalline phosphorus is easily obtained by spontaneous evaporation of the solution in carbon disulfid.

Chemical Properties.—Yellow phosphorus is chemically very active. It combines directly with most of the elements, both positive and negative. A temperature of 40°, the warmth of the hand, or the slightest friction will cause it to inflame. It burns in air or oxygen with great vigor, forming P_2O_5, or, if the supply of air is limited, P_2O_3. It slowly oxidizes and fumes in moist air. In contact with chlorin, bromin, iodin, or nitric acid it bursts into flame. The phosphorescent light which it emits is due to oxidation, and is diminished or prevented by substances which diminish the rapidity of the oxidation (ether, turpentine, ethylene). It does not burn readily in perfectly dry oxygen. Boiled with water it vaporizes with the steam, making it luminous, and this fact is used in the detection of free phosphorus in cases of phosphorus poisoning. When hydrogen is passed over phosphorus, or is evolved from a vessel containing soluble phosphorus compounds, it burns with a green flame which will deposit on a cold plate red phosphorus. The spectrum of phosphorus shows three green lines.

Physiological Properties.—Phosphorus is extremely poisonous. In large doses it causes acute pains, sickness, convulsions, and death. When the vapors arising from it are continuously breathed, they bring on diseases of the bones of the jaws and nose. In very small doses it is medicinal.

Red Phosphorus.—When phosphorus is heated to 240° out of contact with the air, or in a sealed vessel to 300°, it is changed to the red variety, which is as hard as limestone, breaks with a concoidal fracture, and has a specific gravity 1.1. It is usually ground to powder under water and treated with carbon disulfid or caustic soda to remove the unchanged phosphorus. The change to the red variety is also brought about by the action of light or electricity, or at a temperature of 200° in the presence of a very small amount of iodin.

Red phosphorus exhibits many striking differences from yellow phosphorus. It is an amorphous, chocolate-brown powder without taste or smell. It is insoluble in water, carbon disulfid, and other solvents of the yellow variety. It is unchanged in the air, but in moist air oxidizes very slowly. It must be heated to 240° before it ignites. It sublimes at high temperatures, but does not melt at a red heat. It is not luminous in the air and is not poisonous. The

change from yellow to red is exothermic: P yellow = P red +
37,300 cal., and the red is therefore the more stable form.

A third allotrope has been described as *black metallic phos-
phorus*. If phosphorus be heated in a closed tube to 530° it sublimes
and microscopic octahedral crystals are deposited on the wall of
the cooler portions of the tube. If lead and phosphorus be heated
together in a closed tube and after cooling the lead dissolved away
with nitric acid, black, shiny crystals of phosphorus remain which
have a specific gravity 2.34 and are less active than red phos-
phorus.

Illustrations.—To a few cc. of carbon disulfid in a dish add a bit of
phosphorus and note how it dissolves. Dip a strip of paper in the solution
and wave in the air until the CS₂ has evaporated. The finely divided
phosphorus on the surface of the paper takes fire.

Moisten a little pulverized potassium chlorate with the above solution.
In a few minutes the mixture explodes.

To prepare crystals put a gram of phosphorus in a tube, draw out the
open end, exhaust with a Sprengel pump and seal with the blowpipe.
Warm the phosphorus until it melts so that it will adhere to the tube.
Put away in the dark, keeping the upper end of the tube cool and the lower
end warm. This may be done by wrapping the empty end with a rag kept
continually moist. The phosphorus slowly sublimes and crystallizes on the
wall of the tube.

To show the vaporization of phosphorus with steam add a bit to some
water in a small flask closed with a cork through which passes a small
tube. Boil the water in the dark and the escaping steam is luminous.

Pass hydrogen through a tube containing a bit of phosphorus gently
warmed. The hydrogen burns at the end of the tube with a green flame.

If a piece of phosphorus glowing in the air is lowered in a jar of dry
oxygen, or in one containing a few drops of ether, the glowing ceases.

Uses.—Phosphorus is used in medicine, in laboratories, in
the preparation of organic compounds, as a rat poison, and in the
manufacture of matches. For the last purpose one third of the
world's supply is used.

A match is a wooden stick tipped with a mixture which contains
an oxidizing agent, a combustible, and a substance which can be
ignited by friction. The oxidizer is usually potassium chlorate or
nitrate, the combustible is sulfur or paraffin, and the igniting agent
is phosphorus. The stick is first dipped into the melted sulfur or
paraffin, then into a mixture of phosphorus and glue with the
chlorate or nitrate. If chlorate is used the match pops.

Safety matches are tipped with a mixture of potassium chlorate, potassium dichromate, red lead, and antimony sulfid. They are caused to ignite by rubbing them on a rough surface coated with a mixture of red phosphorus and antimony sulfid.

Matches were first made in 1829. They were dipped in sulfur and tipped with a mixture of sugar and potassium chlorate, and were ignited by touching them to sulfuric acid. Friction matches were introduced in 1832, with antimony sulphid as the igniting agent. Phosphorus was first used by Romer of Vienna.

Phosphids.—Phosphorus unites to hydrogen and nearly all the metals to form phosphids. The metallic phosphids may also be regarded as derivatives of hydrogen phosphid, the hydrogen being replaced by the metal. The phosphids are obtained by direct union of the elements or by the action of metals or metallic oxids upon hydrogen phosphid. They are usually brittle solids and many are decomposed by water.

COMPOUNDS OF PHOSPHORUS.

Phosphorus is chemically quite active and forms numerous compounds generally somewhat unstable. It unites directly with both the metals and the non-metals, forms radicals with hydrogen similar to those of nitrogen, and yields acids which form salts with most of the metals. The normal valence is III, but in the acids and salts it is more commonly V.

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.

There are four combinations of phosphorus with hydrogen, one of which is a radical and has not been isolated. They correspond exactly to the similar nitrogen combinationns. They are—

Hydrogen phosphid or Phosphin, PH_3 $\begin{matrix} H \\ H \end{matrix} \!\!>\!\! P\!\!-\!\!H$

Phosphonium, $(PH_4)'$ $\begin{matrix} H \\ H \\ H \\ H \end{matrix} \!\!>\!\! P\!\!-$

Hydrogen diphosphid
  (Liquid hydrogen phosphid), P_2H_4 $\begin{matrix} H \\ H \end{matrix} \!\!>\!\! P\!\!-\!\!P\!\!<\!\! \begin{matrix} H \\ H \end{matrix}$

Hydrogen tetraphosphid
  (Solid hydrogen phosphid), P_4H_2 $\begin{matrix} H\!\!-\!\!P\!\!-\!\!P \\ \quad | \quad | \\ H\!\!-\!\!P\!\!-\!\!P \end{matrix} (?)$

HYDROGEN PHOSPHID, OR PHOSPHIN, PH_3.

Preparation.—Phosphin may be obtained—

1. By the action of water or dilute acids upon alkali phosphids:

$$Ca_3P_2 + 6HCl = 3CaCl_2 + 2PH_3.$$
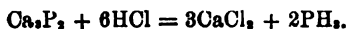
Some liquid P_2H_4 is formed at the same time.

2. By the action of water or alkali hydroxids upon phosphonium iodid:

$$PH_4I + H_2O = HI + H_2O + PH_3.$$

3. By the action of alkali hydroxids and water upon phosphorus:

$$3NaHO + 3H_2O + 4P = 3NaH_2PO_2 + PH_3.$$
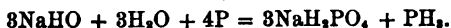
In this reaction some liquid P_2H_4 is formed and hydrogen is also set free through the decomposition of the sodium hyposulfite by the alkali.

4. By heating phosphites or hypophosphites :

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$
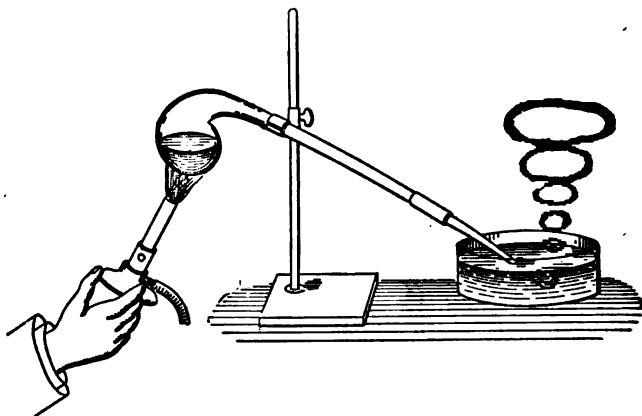
FIG. 63.

Hydrogen phosphid is most conveniently prepared by the third reaction. Strong solution of potassium or sodium hydroxid is placed with a few small pieces of phosphorus in a small retort furnished with a delivery-tube which dips under water. The flask is filled with carbon dioxid or coal gas and then gently heated. As the bubbles of gas rising to the surface of the water come in contact with the air, they burst into flame, making beautiful white rings of P_2O_5. By conducting the gas through a tube immersed in a freezing mixture, it is freed from liquid P_2H_4 and is no longer spontaneously inflammable. It is still mixed with some hydrogen.

Physical Properties.—Hydrogen phosphid is a colorless gas with an unpleasant, garlic-like odor, and has a specific gravity 1.185. It is slightly soluble in water, alcohol, and ether. Its aqueous solu-

tion is luminous and on exposure to air and light deposits amorphous phosphorus. It becomes liquid at $-85°$ and solid at $-133.5°$. It is very poisonous and should be handled with great care.

Chemical Properties.—Hydrogen phosphid is unstable and very active. It takes fire at $100°$ and burns to P_2O_5 and H_2O, which unite at once to form phosphoric acid, H_3PO_4. Its mixture with oxygen is violently explosive. It is decomposed by heat and electricity and in contact with nitric acid, chlorin, bromin, iodin, or sulfur. Its heat of formation is $(PH_3) = 36,600$ cal.

PHOSPHONIUM COMPOUNDS.

Phosphin is the analogue of ammonia, and like it unites directly to the haloid acids to form phosphonium halids, $PH_3 + HCl = PH_4Cl$. The radical PH_4, called phosphonium, corresponds to the ammonium radical, but forms few compounds, since it does not seem to be able to unite with acid radicals which contain oxygen. It forms double haloid salts with aluminum, tin, titanium, and antimony. Phosphonium salts are decomposed by water or alkalis:

$$PH_4I + H_2O = HI + H_2O + PH_3,$$

and hence solutions cannot be obtained. The radical has not been isolated.

Phosphonium Chlorid, PH_4Cl, is formed when a mixture of phosphin and hydrogen chlorid is subjected to a pressure of 18 atmospheres or lowered in temperature to $-25°$. It is a white solid which sublimes and condenses in cubical crystals. As soon as the pressure is relieved or the temperature raised dissociation takes place.

Phosphonium Bromid, PH_4Br, is obtained by bringing phosphin and hydrogen bromid together in a cooled vessel. It forms white cubical crystals which melt with decomposition at $30°$.

Phosphonium Iodid, PH_4I, may be prepared in the same manner as PH_4Br, or by the action of water upon a mixture of phosphorus and iodin:

$$9I + 13P + 24H_2O = 2HI + 6H_3PO_4 + 7PH_4I.$$
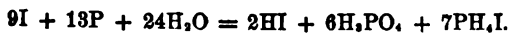
Two parts of phosphorus are dissolved in carbon disulfid in a retort and three and a half parts of iodin added. The CS_2 is distilled off. the vessel being kept full of carbon dioxid, then six parts of water are added through a dropping-funnel. The PH_4I distils over and is condensed in a receiver or long tube. It forms colorless lustrous quadratic prisms.

Phosphonium Hydroxid, PH_4OH. When PH_3 dissolves in water there is possibly formed PH_4OH, but if so it is unstable and cannot be isolated.

HYDROGEN DIPHOSPHID.

Hydrogen Diphosphid, P_2H_4, or *liquid hydrogen phosphid*, is formed at the same time with phosphin by the action of potassium hydroxid upon phosphorus, and in larger quantities by the action of water upon calcium phosphid. Calcium phosphid is placed in a flask, the air displaced by an inert gas, and water added through a dropping-funnel. The gases are passed through a strongly cooled U-tube in which the P_2H_4 condenses. It is a colorless, highly refractive liquid which boils at 80° and is insoluble in water. It takes fire in the air and makes combustible gases with which it may be mixed spontaneously inflammable. It is decomposed by light and many chemical agents into phosphin and solid hydrogen phosphid.

Hydrogen diphosphid is the analog of hydrazin, but is too weakly basic to form salts.

HYDROGEN TETRAPHOSPHID.

Hydrogen Tetraphosphid, P_4H_2, or as it is commonly called, *solid hydrogen phosphid*, is a yellow powder formed by decomposition of hydrogen diphosphid, or by the action of chlorin upon phosphin, or by the action of hydrochloric acid upon calcium phosphate. It inflames at 160° and is decomposed by concussion.

HALIDS OF PHOSPHORUS.

Phosphorus forms tri and penta halids, and also mixed compounds such as PF_2Cl_3 and PBr_2Cl_3. The pentaiodid has not been prepared, but we have instead the radical PI_2 or P_2I_4. These compounds are all formed by direct union of their constituents in proper proportion. The fluorids may be more conveniently prepared by action of the chlorids of phosphorus upon the fluorids of arsenic and zinc. In preparing the bromids and iodids it is best to dissolve the phosphorus first in carbon disulfid.

The phosphorus halids are all exothermic and some of them are quite stable, but they are at the same time very energetic chemical agents because of the activity of their constituents. The stability increases as the atomic weight of the halogen diminishes. The pentaiodid cannot be formed, while the pentafluorid can be gasified without decomposition. They unite with many other compounds, making double salts. They have the faculty, particularly the chlorids, of replacing with the halogen the hydroxyl of acids, both organic and inorganic, and of alcohols. They are all decomposed by water with formation of the haloid acid and an acid of phos-

phorus. .They are much used as chemical agents, particularly in the preparation of organic compounds.

The heat of formation is shown in the following:

$(P,Cl_3) = 75,500$ cal. $(P,Cl_5) = 105,100$ cal. $(P,Br_3) = 44,800$ cal.
$(P,Br_5) = 59,100$ cal. $(P,I_3) = 10,900$ cal. $(P_2,I_4) = 19,800$ cal.

Phosphorous Fluorid (Phosphorus trifluorid), PF_3, is a colorless gas which liquefies under 40 atmospheres at 10°. It attacks glass when warmed, is decomposed by heat and the electric spark, and unites directly to bromin to form PBr_3F_2.

Phosphoric Fluorid (Phosphorus pentafluorid), PF_5, is a heavy colorless strong-smelling gas which is liquid at 15° under 46 atmospheres. It fumes in the air, irritates the mucous membranes, and attacks moistened glass.

Phosphorous Chlorid (Phosphorus trichlorid), PCl_3, is a colorless highly refractive liquid of specific gravity 1.6 It boils at 76° and does not liquefy at − 115°. It fumes strongly in the air, has a pungent odor, and unites directly to chlorin to form PCl_5.

Phosphoric Chlorid (Phosphorus pentachlorid), PCl_5, is prepared by the union of dry chlorin with PCl_3, or by passing chlorin into a solution of phosphorus in carbon disulfid kept cold. It is a yellowish-white solid which crystallizes in rhombic plates. It fumes in the air, melts at 148° under pressure, boils with decomposition at 160°, sublimes without melting, and dissociates completely at 300° into PCl_3 and Cl_2.

Phosphorus Chlorofluorid, PCl_3F_2, is a colorless gas which liquefies at −8°.

Phosphorous Bromid (Phosphorus tribromid), PBr_3, is a colorless fuming liquid which boils at 175° and has a specific gravity 2.7.

Phosphoric Bromid (Phosphorus pentabromid), PBr_5, is a yellow fuming crystalline solid which melts to a red liquid and dissociates at 100° into PBr_3 and Br_2.

Phosphorus Bromofluorid, PBr_2F_3, is a fuming liquid which is decomposed by water with violence.

Phosphorus Bromochlorid, PBr_2Cl_3, a yellow crystalline solid, melts at 35°.
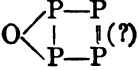
Phosphorous Iodid (Phosphorus tri-iodid), PI_3, is an unstable deliquescent solid which crystallizes in red six-sided prisms and melts at 55°.

Phosphorus Tetraiodid, P_2I_4, is a yellow crystalline solid which melts at 110°.

Phosphorus Iodochlorid, PI_2Cl_3, forms large red deliquescent six-sided crystals.

<div align="center">OXIDS OF PHOSPHORUS.</div>

There are four oxids of phosphorus as follows:

Phosphorus monoxid, P_4O $O{\Large\langle}\begin{array}{c}P—P\\ |\quad\ |\\ P—P\end{array}(?)$

Phosphorous oxid, $P_2'''O_3$ $O=P—O—P=O$

Phosphorus tetroxid, $P_2^vO_4$ $\begin{smallmatrix}O\\O\end{smallmatrix}\!\!>\!\!P—P\!<\!\begin{smallmatrix}O\\O\end{smallmatrix}$

Phosphoric oxid, $P_2^vO_5$ $O=P—O—P=O$
                                    $\begin{smallmatrix}|\\O\end{smallmatrix}$ $\begin{smallmatrix}|\\O\end{smallmatrix}$
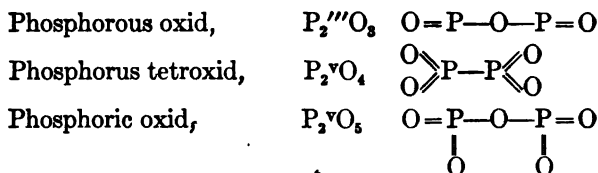
The oxids P_2O_3 and P_2O_5 are regular and unite to water to form acids. P_4O may be a mixture or may have the formula suggested. P_2O_4 is either a radical or a combination of trivalent and pentavalent phosphorus with oxygen, thus: $O=P—O—P\!<\!\begin{smallmatrix}O\\O\end{smallmatrix}$. The hypophosphorus oxid P_2O has not been prepared.

All these oxids are formed by the oxidation of phosphorus, P_2O_5, when the supply of oxygen is abundant and the others when the supply is limited. They are all exothermic. The heat of formation of P_2O_5 is 369,900 calories.

PHOSPHOROUS OXID (PHOSPHORUS TRIOXID).

Formula P_2O_3 or P_4O_6. Molecular weight 110 or 220. Density 110.

Preparation.—Phosphorous oxid is obtained along with the higher oxids when phosphorus burns with a limited supply of air. To prepare it, place a piece of phosphorus in one end of a tube, the other end of which is attached to an aspirator. Pass a slow current of air and warm the phosphorus. The P_2O_3 condenses in the cooler portion of the tube. To separate it from the P_2O_5 which is formed at the same time, connect the tube with a condenser surrounded with water at 60°. The P_2O_5 is condensed and the P_2O_3 passes over and may be collected in a well-cooled U-tube.

Physical Properties.—Phosphorous oxid is a white feathery crystalline solid which melts at 22.5°, sublimes easily, boils at 173°, and decomposes at 300° into phosphorus and the tetroxid. The liquid solidifies at 21°, forming monoclinic prisms. It has an unpleasant, garlic-like odor, and is quite poisonous. Its density is 110, indicating a molecular formula P_4O_6.

Chemical Properties.—Phosphorous oxid dissolves slowly in cold water to form phosphorous acid, H_3PO_3, while with hot water it yields hydrogen phosphid and red phosphorus. It dissolves in benzene, carbon disulfid, and chloloform. It burns to P_2O_5 and inflames spontaneously in warm air or chlorin.

PHOSPHORIC OXID (PHOSPHORUS PENTOXID).

Formula P_2O_5.   Molecular weight 126.

Preparation.—Phosphoric oxid is formed by the combustion of phosphorus in an abundant supply of air or oxygen.   Ignite a bit of phosphorus in a capsule on a plate and invert over it a bell glass. Dense clouds of P_2O_5 fill the bell, and gathering together in flakes, fall upon the plate.   For preparation on a larger scale air or oxygen is drawn through a glass globe into which pieces of phosphorus are dropped.   A capsule receives the phosphorus and must be warmed at the beginning of the operation.

Illustration.—The formation of P_2O_3, P_2O_5, and red phosphorus may be shown in one simple experiment.   Place in the middle of an open tube, about 30 cm. long and 1 cm. in diameter, a small piece of phosphorus and warm gently.   The phosphorus takes fire, but soon consumes the air in its immediate neighborhood. P_2O_5 condenses near the phosphorus, P_2O_3 further on, and a portion of the phosphorus is converted into red phosphorus.   By inclining the tube so as to create a current of air the P_2O_3 may be made to burn with a pale-yellow flame at the end of the tube.

Physical Properties.—Phosphoric oxid is a bulky white amorphous odorless solid which deliquesces strongly in the air.   It usually has an odor due to the presence of a little P_2O_3.   If carefully heated to 250° it sublimes or volatilizes, but above this changes to a polymer which is a gas only at a white heat.

Chemical Properties.—Phosphoric oxid dissolves in water with a hissing sound to form phosphoric acid.   It has a strong attraction for moisture, and is one of the most powerful drying agents known to the chemist.   When not pure it has a reducing action because of the presence of phosphorus or its lower oxids.

Phosphorus Monoxid, P_4O.—When phosphorus is burned in a tube in a slow current of air an orange-red solid is obtained to which the formula P_4O has been given.

Phosphorus Tetroxid, P_2O_4.—This compound is said to be obtained when P_2O_3 is heated in a closed tube to 440°.   It forms a transparent crystalline sublimate on the tube.

ACIDS OF PHOSPHORUS.

Phosphorus forms six acids as follows:

Hypophosphorous acid; $H_3P'''O_2$ $\begin{matrix} H-O \\ H-O \end{matrix}\Big\rangle P-H$

Phosphorous acid, $H_3P'''O_3$　$\begin{array}{l} H-O \\ H-O \\ H-O \end{array}\!\!\!\searrow\!P$

Diphosphorous acid (Pyrophosphorous acid), $H_4P_2O_5$　$\begin{array}{l} H-O \\ H-O \end{array}\!\!\!\searrow\!P-O-P\!\!\!\nwarrow\begin{array}{l} O-H \\ O-H \end{array}$

Orthophosphoric acid (Monometaphosphoric acid), $H_3P^VO_4$　$\begin{array}{l} H-O \\ H-O \\ H-O \end{array}\!\!\!\searrow\!P=O$

Pyrophosphoric acid (Diphosphoric acid), $H_4P_2^VO_7$　$\begin{array}{l} H-O \\ H-O \end{array}\!\!\!\searrow\!\underset{\overset{\|}{O}}{P}-O-\underset{\overset{\|}{O}}{P}\!\!\!\nwarrow\begin{array}{l} O-H \\ O-H \end{array}$

Metaphosphoric acid (Dimetaphosphoric acid), HP^VO_3　$H-O-P\!\!\!\nwarrow\begin{array}{l} O \\ O \end{array}$
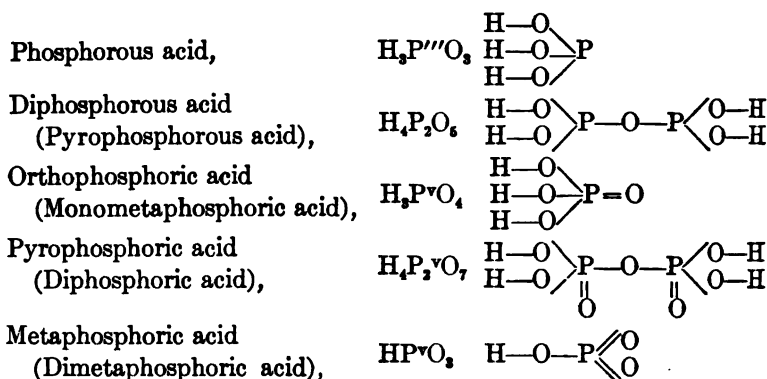
These acids have a tendency to act with a basicity less than the number of hydrogen atoms. This is due to the way in which they ionize. We have from the first only the ion H_2PO_2', and from the second the ions H_2PO_3' and HPO_3'', but not PO_3'''. The fourth yields successively with increasing difficulty the ions H_2PO_4', HPO_4'', and PO_4'''. The salts are generally alkaline because of hydrolysis, which liberates the hydroxyl ion. Sodium phosphate decomposes in solution as follows:

$$Na_3\cdot,PO_4''' + H_2O = 2Na\cdot_2,HPO_4'' + Na\cdot,HO'.$$
$$Na_2\cdot,HPO_4'' + H_2O = Na\cdot,H_2PO_4' + Na\cdot,HO'.$$
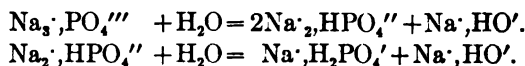
The heat of formation of the phosphate ions is $H_2PO_4' = 308,600$ cal., $HPO_4'' = 307,300$ cal., $PO_4''' = 300,600$ cal.

HYPOPHOSPHOROUS ACID.

Formula H_3PO_2, or HPO,H_2O.　Molecular weight 66.

Preparation.—By the action of barium or sodium hydroxid on phosphorus, phosphine and a salt of hypophosphorous acid are formed:

$$8P + 3BaH_2O_2 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3.$$
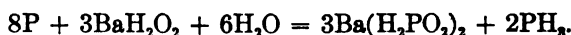
The acid is separated from the barium salt by sulfuric acid:

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2.$$
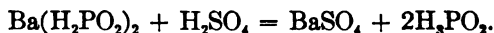
The barium sulfate is filtered off and the solution concentrated in vacuo.

Properties.—Hypophosphorous acid is a colorless liquid which freezes at 0°, forming large white leaflets which melt at 17.4°. When heated it dissociates into phosphoric acid and phosphine. It acts as a powerful reducing agent because of its tendency to

absorb oxygen and become phosphoric˘acid. It is a monobasic acid and may be a molecular union of HPO and water. Its heat of formation is, liquid 137,660 cal., solid 139,970 cal., solution 139,800 cal.

Hypophosphites.—Many of the metals form hypophosphites which are mostly crystalline salts. They are decomposed by heat, yielding phosphine, hydrogen, and a pyro or metaphosphate. They are easily oxidized to phosphites and phosphates and are hence reducing agents.

Ammonium Hypophosphite, $NH_4H_2PO_2$, crystallizes in hexagonal tablets.

PHOSPHOROUS ACID.

Formula H_3PO_3.   Molecular weight 82.

Preparation.—Phosphorous acid is formed—

1. By union of phosphorus oxid and water:
$$P_2O_3 + 3H_2O = 2H_3PO_3.$$
2. By the slow oxidation of phosphorus in moist air.
3. By the action of water upon phosphorus chlorid:
$$3H_2O + PCl_3 = 3HCl + P(OH)_3.$$
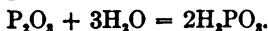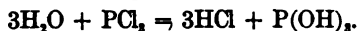
In preparing it by the last reaction chlorin is passed through phosphorus melted under water. As fast as the trichlorid is formed it is decomposed by the water. The current of chlorin must be stopped before the phosphorus is all consumed, otherwise the phosphorus is oxidized to phosphoric acid. The solution is evaporated at 180° to a thick syrup which crystallizes on cooling.

Properties.—Phosphorous acid is a deliquescent solid with a garlic-like odor and taste. It melts at 70.1° and at higher temperatures decomposes into phosphin and phosphoric acid. It absorbs oxygen readily, becoming a phosphoric acid, and thus acts as a reducing agent. Although it probably contains three hydroxyls, it acts only as a dibasic acid.

Diphosphorous acid, $H_4P_2O_5$, has been prepared by shaking H_3PO_3 with PCl_3 at 35°. Dried in a desiccator over P_2O_5 and KHO, it forms deliquescent crystals which melt at 38°. It dissolves in water to H_3PO_3 and decomposes at 100°, yielding H_3P.

Phosphites.—The phosphites are crystalline salts with taste like the acid. They are decomposed by heat and not easily oxidized..

Ammonium Phosphites, $NH_4H_2PO_3$ and $(NH_4)_2HPO_3$, $2H_2O$, are obtained as crystalline solids by the action of ammonia upon phosphorous acid.

ORTHOPHOSPHORIC ACID (MONOMETAPHOSPHORIC ACID).

Formula H_3PO_4. Molecular weight 98.

Preparation.—Orthophosphoric acid is formed—

1. By dissolving phosphoric oxid in hot water:
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$
2. By the action of water upon PCl_5 or $POCl_3$:
$$PCl_5 + 4H_2O = 5HCl + H_3PO_4.$$
3. By the oxidation of phosphorus with nitric acid in a complicated reaction.
4. By the action of sulfuric acid upon calcium phosphate or bone ash:
$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

Commercial phosphoric acid is usually prepared by the last method. It frequently contains arsenic, from which it may be freed by passing through it sulfurous oxid and precipitating the reduced arsenic with hydrogen sulfid.

Properties.—Phosphoric acid mixes with water in all proportions, making a solution which has a pleasant acid taste and whose strength is indicated by its specific gravity.

When the solution is concentrated until the temperature rises to 140° and then cooled, the acid crystallizes out in six-sided rhombic prisms which terminate in six-sided pyramids, and have a specific gravity 1.88. It melts at 38.6° and at 160° begins to decompose into water and diphosphoric acid. Its silver salt is yellow. The heat of formation of the solid acid is 302,600 calories.

Orthophosphates.—Orthophosphoric acid is tribasic and forms acid, normal, and double salts. With alkali metals it usually retains one or more hydrogen atoms, and when only one remains the salt is alkaline because of the strong basic character of these metals. With other metals the three hydrogen atoms are usually replaced. Double salts are very common. Examples of these phosphates are calcium phosphate, $Ca_3(PO_4)_2$, hydrogen disodium phosphate, HNa_2PO_4, dihydrogen potassium phosphate, H_2KPO_4, and hydrogen sodium ammonium phosphate, $HNaNH_4PO_4$ (microcosmic salt).

Orthophosphates in ammoniacal solution are precipitated by magnesium sulfate as ammonium magnesium phosphate, NH_4MgPO_4, and are thus recognized and quantitatively determined.

Ammonium Orthophosphates.—There are three salts:

Monammonium phosphate, $NH_4H_2PO_4$, square prisms, specific gravity 1.7.

Diammonium phosphate, $(NH_4)_2HPO_4$, monoclinic prisms, specific gravity 1.6.

Triammonium phosphate, $(NH_4)_3PO_4$, $3H_2O$, short pyramids.

Chromium Orthophosphates.—Chromic orthophosphate has two forms, $Cr_2P_2O_8$, $12H_2O$, violet crystals, and $Cr_2P_2O_8$, $6H_2O$, green crystals.

Chromous orthophosphate, $Cr_3P_2O_8$, H_2O, is a blue solid.

DIPHOSPHORIC ACID (PYROPHOSPHORIC ACID).

Formula $H_4P_2O_7$. Molecular weight 147.

Preparation.—Diphosphoric acid is formed by heating the ortho acid to 213° until its solution gives a white precipitate with silver nitrate, or by the union of the ortho and meta acids in molecular proportions: $H_3PO_4 + HPO_3 = H_4P_2O_7$.

Properties.—Diphosphoric acid is an opaque white crystalline solid. Its aqueous solution passes to the ortho acid, slowly in the cold, rapidly when heated.

Diphosphates or **Pyrophosphates.** — Although diphosphoric acid is tetrabasic, only two series of salts are formed, since the hydrogen atoms are replaced in pairs. For example, we have $H_2Na_2P_2O_7$ and $Na_4P_2O_7$, the first slightly acid and the second alkaline. The diphosphates are obtained by heating the mono-hydrogen orthophosphates. The salts of the alkalis are soluble, while the others are insoluble, in water.

Ammonium Diphosphates, $(NH_4)_4P_2O_7$ and $H_2(NH_4)_2P_2O_7$, are formed by the action of ammonia upon diphosphoric acid.

Chromium Diphosphate, $Cr_4(P_2O_7)_3$, is obtained as a green precipitate by adding $Na_4P_2O_7$ to chrome alum solution.

METAPHOSPHORIC ACID (DIMETAPHOSPHORIC ACID).

Formula HPO_3. Molecular weight 80.

Preparation.—Metaphosphoric acid is obtained by dissolving phosphoric oxid in cold water: $H_2O + P_2O_5 = 2HPO_3$; or by heating ortho or diphosphoric acid to 400°.

Properties.—Metaphosphoric acid is a glassy transparent deliquescent solid called *glacial phosphoric acid.* It melts above 400° and vaporizes at a red heat. It forms an aqueous solution which precipitates albumen, a fact which serves to distinguish it from the other phosphoric acids. Its solution changes slowly in the cold, rapidly when heated, into H_3PO_4.

Metaphosphates.—Metaphosphoric acid is monobasic and can form only normal salts. These are obtained by the action of metals on the acid, or by heating the dihydrogen ortho salts: $NaH_2PO_4 = NaPO_3 + H_2O$. With boiling water this action is reversed. They give a white precipitate of silver phosphate.

Tests.—The three phosphoric acids may be distinguished as follows:

Metaphosphoric acid coagulates albumen and makes a white gelatinous precipitate with silver nitrate.

Diphosphoric acid has no action on albumen and makes a white crystalline precipitate with silver nitrate.

Orthophosphoric acid has no action on albumen, gives a yellow precipitate with silver nitrate, and a yellow precipitate of ammonium phosphomolybdate with solution of ammonium molybdate in nitric acid.

OXYHALIDS OF PHOSPHORUS.

Phosphoric Oxyfluorid, POF_3, is formed by the action of P_2O_5 upon fluorids. It is a fuming gas which liquefies at − 50°, or at 16° under 15 atmospheres, and at low temperatures is a snow-like solid.

Phosphoric Oxychlorid (Phosphoryl chlorid), $POCl_3$, is obtained by the action of PCl_5 upon water or P_2O_5, or by heating PCl_5 with oxalic or boric acid:

$$3PCl_5 + 2H_3BO_3 = 6HCl + B_2O_3 + 3POCl_3.$$

It is a colorless, fuming, highly refractive liquid which boils at 107° and at − 10° becomes a white crystalline solid which melts at 1°. With water it forms orthophosphoric and hydrochloric acids:

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$
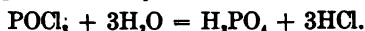
Diphosphoric Oxychlorid (Pyrophosphoryl chlorid), $P_2O_3Cl_4$, is formed by passing NO_2 through PCl_3. It is a colorless, fuming liquid which boils at 210° and with water yields orthophosphoric acid. Its vapor attacks the eyes and nose. Specific gravity 1.78.

Phosphoric Oxybromid (Phosphoryl bromid), $POBr_3$, is obtained by the action of Br upon moist air or oxalic acid. Colorless plates which melt at 55° and boil at 195°.

Phosphoric Oxybromchlorid, POBrCl₂, is a colorless liquid which solidifies at 0° to tablets which melt at 11°.

COMPOUNDS OF PHOSPHORUS AND SULFUR.

Several compounds of phosphorus and sulfur have been described, only two of which are regular. The others are either radicals or mixtures. They are all formed by heating phosphorus and sulfur together in the proportions indicated by the formulas.

Phosphorus Monosulfid, P_4S, a heavy, oily liquid, very inflammable.
Phosphorus Disulfid, P_4S_3, a yellow, fuming, inflammable liquid.
Phosphorus Trisulfid, P_4S_3, a yellow crystalline solid, melts at 142°.
Phosphorous Sulfid (Phosphorus trisulfid), P_2S_3, or P_4S_6, a colorless, odorless, tasteless, crystalline solid which melts at 200°, sublimes above this, and boils at 490°.
Phosphoric Sulfid (Phosphorus pentasulfid), P_2S_5, a yellow crystalline solid, melts at 274°, boils at 520°, is decomposed by water. It is used in preparing many organic compounds.

Thiophosphates.—There are several phosphates in which oxygen is partially or wholly replaced by sulfur; as sodium thioxyphosphate, Na_3PSO_3, $12H_2O$, and sodium thiophosphate, Na_3PS_4.

Thiohalids.—Phosphorus forms with fluorin, chlorin, and bromin thiohalids, as $PSCl_3$; also mixed thiohalids, as phosphorus thiobromchlorid, $PSBrCl_2$.

PHOSPHORUS WITH SELENIUM AND TELLURIUM.

There are four selenids of phosphorus: P_4Se, a yellow, bad-smelling liquid; P_4Se_3, a red solid; P_2Se_3, a ruby-red liquid; and P_2Se_5, a red crystalline solid.

There are a few selenphosphates in which selenium replaces oxygen.
Tellurium forms one or two phosphids and a few other compounds.

COMPOUNDS OF PHOSPHORUS WITH NITROGEN.

There is small affinity between phosphorus and nitrogen, and yet they exist together in many molecules. These compounds may be regarded as derivatives of ammonia or as amidogen derivatives of phosphoric acid. Examples are:

Phospham, $P^vN(NH)$, or $N \equiv P = N - H$, is obtained by the action of PCl_5 upon ammonia. It is a light, white powder, insoluble in water and infusible below a red heat.

Phosphamid, $P^vO(NH)NH_2$, or $O = P\diagup\diagdown$, is obtained as a white insoluble powder by the action of water upon phospham.

ARSENIC.

Symbol As. Atomic weight 75. Density 150. Molecular weight 300. Molecular formula As_4. Specific gravity 5.64 to 5.96. Melting-point 500°.

Occurrence.—Arsenic is found free in small quantities in nodules or crystals. Combined it occurs in various forms: as sulfids in realgar, As_2S_2, and orpiment, As_2S_3; as arsenids of iron, $FeAs_2$ and Fe_4As_3, of nickel, NiAs and $NiAs_2$, of cobalt, $CoAs_2$; as mixed compounds, arsenical pyrites, FeAsS; cobalt glance, CoAsS; nickel glance, NiAsS; also as the oxid As_2O_3, and as arsenates. It occurs as an impurity in many ores, especially the sulfids, and hence is found in sulfuric acid made from pyrites. It is a constituent of sea-water and many mineral waters.

History.—The sulfids of arsenic were known to the ancients. They were called by Aristotle *sandarache,* and by Theophrastus *arsenikon.* Arsenous oxid was known to Geber, Valentine, and Albertus Magnus. The element was first obtained by Schröder in 1694, and the composition of arsenous oxid was ascertained by Brandt in 1773.

Preparation.—Arsenic is prepared—

1. By subliming the native arsenic.
2. By heating arsenous oxid with charcoal:

$$2As_2O_3 + 3C = 3CO_2 + As_4.$$
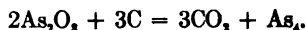
3. By roasting arsenical pyrites: FeAsS = FeS + As.

Commercial arsenic is usually obtained by the last method. The ore is heated in earthenware cylinders, into the mouths of which are inserted cylinders of sheet iron. The arsenic sublimes into the iron cylinders, from which it is removed by unrolling the sheet. To purify it, it is resublimed with charcoal.

Physical Properties.—Arsenic is a brittle steel-gray metal-like solid which crystallizes in rhombohedrons. It has a specific gravity 5.64 to 5.96 and specific heat 0.083. It is insoluble in water, alcohol, and ether. It is volatile above 100°, sublimes rapidly at 400°, and melts only under pressure. Its vapor has a lemon-yellow color and a disagreeable garlic-like odor. Its density is 150 at 860°, indicating a molecular formula, As_4. At higher temperatures it dissociates, until at 1736° its density is only 160.

Arsenic exists in at least two allotropic modifications, the one

just described, and another which is called *amorphous arsenic.*
The latter is formed when arsenic is sublimed and suddenly cooled,
or when hydrogen arsenid is decomposed by heat. It is a black
amorphous lustrous powder of specific gravity 4.71.   At 360° it
reverts to the crystalline form.

Chemical Properties.—Arsenic is quite active and forms a large
number of compounds. It tarnishes in moist air and ignites at 180°,
burning to As_2O_3. (Amorphous arsenic remains unchanged in the
air.)   It is oxidized by nitric and sulfuric acids and its oxids are
reduced by hydrogen sulfid. It inflames spontaneously in chlorin
and bromin.   It combines directly with most elements and its acids
form numerous salts.   It is a non-metal, but in its physical proper-
ties it is quite metallic and in some of its chemical actions it is basic.
In many of its compounds with the metals it shows a striking resem-
blance to sulfur.

Illustrations.—The sublimation of arsenic and the two allotropic
forms may be shown by heating a fragment in a tube through which
a current of hydrogen is passing.   That which condenses near the heated
portion of the tube is crystalline, while that deposited further on is
amorphous.

Physiological Properties.—All the soluble compounds of arsenic
are violent poisons and its detection becomes often a matter of
great importance in medico-legal procedures.   The tests will be.
given later.   Some of its compounds are useful medicines.   ·

Uses.—Arsenic forms alloys with many metals.   It is added
to lead from which shot are to be made because this alloy assumes
the spheroidal form better than pure lead as it falls from the
shot-tower.   Some of its compounds, as London purple, Paris green,
and arsenous oxid, are much used as poisons for the destruction of
insects and vermin.

Arsenids.—Arsenic is not very strongly negative and hence
forms rather weak and not very definite compounds with the
metals.   Indeed, many of them are alloys rather than compounds,
and the union is made in varying proportions without much regard
to valence.   We have, for example, native copper arsenids as
follows: *Domeykite,* Cu_3As, *Algodonite,* Cu_6As, and *Darwinite,* Cu_9As.
The arsenids and alloys are usually brittle solids and are of but little
commercial value.

ARSENIC COMPOUNDS.

Arsenic forms numerous compounds, mainly resembling those of phosphorus. It forms arsenous and arsenic compounds with valences III and V, but the elemental ions do not readily separate. The arsenites and arsenates resemble the corresponding phosphorus compounds and the acid ions have a tendency to retain the hydrogen.

Some of the thermal equations are as follows:

$(As_2,O_3) = 154,700$ cal. $(As_2O_3,Aq.) = -7,600$ cal.

$(H_3,As) = -44,100$ cal. $(As,Cl_3) = 71,500$ cal.

$(As,Br_3) = 44,900$ cal. $(As,I_3) = 12,700$ cal.

$(As_2,O_5) = 219,400$ cal. $(H_3,As,O_3) = 147,100$ cal.

$(H_3,As,O_4,Aq.) = 215,300$ cal.
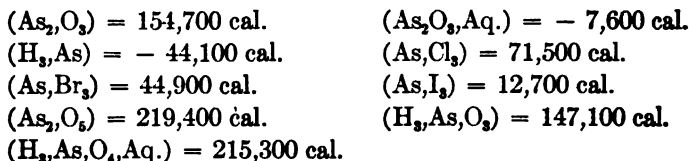
COMPOUNDS OF ARSENIC WITH HYDROGEN.

Arsenic forms three compounds with hydrogen: A gas, H_3As; a solid, H_2As_2 or $H—As = As—H$, and a hypothetical compound, H_4As_2 or $\frac{H}{H} > As—As < \frac{H}{H}$, corresponding to hydrazin. The last has not been separated, but its derivatives are known, the most familiar of which is the organic compound called *cacodyl*, $As_2(CH_3)_4$.

HYDROGEN ARSENID (ARSIN).

Formula H_3As. Molecular weight 78. Density 39.

Preparation.—Hydrogen arsenid is formed—

1. By the action of dilute acids upon zinc arsenid:

$$As_2Zn_3 + 3H_2SO_4 = 3ZnSO_4 + 2H_3As.$$
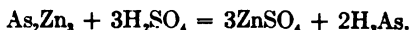
2. By the action of nascent hydrogen, as when a compound of arsenic is added to a vessel from which hydrogen is being evolved:

$$As_2O_3 + 6H_2 = 3H_2O + 2H_3As.$$
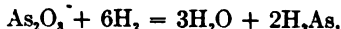
3. In the reduction of arsenic compounds by decaying organic matters. It may thus occur in rooms covered with arsenical wall-paper.

Properties.—Hydrogen arsenid is a colorless poisonous gas with a garlic-like odor. It condenses to a liquid which melts at $-55°$ and it becomes a white crystalline solid at $-114°$. It is slightly soluble in water and the solution deposits arsenic on exposure to the air. It burns with a bluish-white flame to water and arsenous oxid. If the flame is cooled by holding in it a porcelain

plate, black metallic arsenic is deposited. It makes an explosive mixture with oxygen. It is less stable than ammonia and phosphin, is easily decomposed by heat and chemical reagents, and is a reducing agent. It acts with the halogens to form the halid of arsenic and the haloid acid. It precipitates silver from silver nitrate and copper arsenid from copper sulfate.

Arsonium Compounds.—Hydrogen arsenid is not strongly alkaline like ammonia and phosphin. Arsonium hydroxid, AsH_4OH, has not been isolated, but its derivatives, as well as those of hydrogen arsenid, are numerous. In them the hydrogen atoms are usually all replaced. There are many compounds which contain organic radicals, such as methyl arsindichlorid, $As(CH_3)Cl_2$. /

Marsh's Test for Arsenic.—The common method of détecting arsenic is that of Marsh. Into a vessel from which hydrogen is being evolved by means of zinc and sulfuric acid the liquid to be examined is introduced. If arsenic is present, the nascent hydrogen converts it into H_3As and this gas passes out with the hydrogen. On igniting the jet and holding a white porcelain plate in the flame, a black spot of amorphous arsenic is produced. If the tube through which the gas is passing be heated, a mirror of arsenic is deposited. Antimony makes a similar spot. but is distinguished easily, since the arsenic is soluble in calcium hypochlorite, while antimony is not.
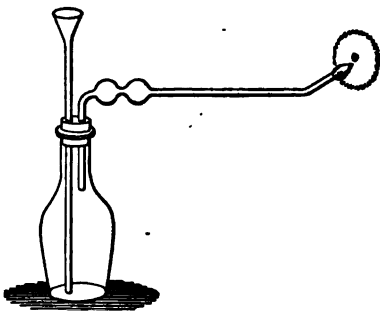
FIG. 64.

Solid Hydrogen Arsenid, H_2As_2, is formed by the action of potassium or sodium arsenid on water. It is a soft unstable brown powder.

HALIDS OF ARSENIC.

Arsenic forms all the trihalids and pentahalids of chlorin and iodin. These compounds are formed by direct union of the elements or by the action of halids upon arsenic and its compounds.

Arsenous Fluorid, AsF_3, is a colorless fuming liquid of specific gravity 2.73. It boils at 61°, etches glass and decomposes water.

Arsenous Chlorid, AsCl₃, is a colorless fuming oily liquid of specific gravity 2.2. It is solid at −30° and boils at 134°. With water it yields arsenous hydroxychlorid, As(HO)Cl₂, as well as the oxychlorid AsOCl.

Arsenic Chlorid, AsCl₅, is formed by union of AsCl₃ with Cl at −35°

Arsenous Bromid, AsBr₃, is a colorless deliquescent crystalline solid of specific gravity 3.66. It melts at 20° and boils at 220°. With water it yields arsenous oxybromid, AsOBr.

Arsenous Iodid, AsI₃, forms red hexagonal crystals.

Arsenic Iodid, AsI₅, is a brown crystalline solid.

OXIDS OF ARSENIC.

There are two oxids of arsenic, both of which form acids:

$$\text{Arsenous oxid,} \quad As_2'''O_3 \quad O=As\!-\!O\!-\!As=O$$

$$\text{Arsenic oxid,} \quad As_2^VO_5 \quad O=As\!-\!O\!-\!As=O$$
$$\underset{O}{\overset{\shortparallel}{}} \qquad \underset{O}{\overset{\shortparallel}{}}$$
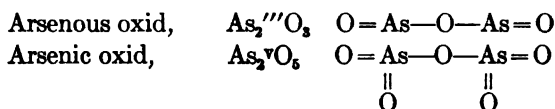
ARSENOUS OXID.

Formula As₂O₃ or As₄O₆. Molecular weight 198 or 396. Density 198.

Preparation.—Arsenous oxid is commonly known as *arsenous acid* or *white arsenic* or simply *arsenic*. It is prepared on a large scale by roasting arsenical pyrites with free access of air, or as a by-product in the reduction of arsenic-bearing ores. The oxid formed volatilizes and is condensed in large chambers. It is also obtained by burning arsenic in air or oxygen, or by oxidizing the metal with nitric acid. It is purified by sublimation.

Physical Properties.—Arsenous oxid has three allotropic modifications:

1. *Octahedral arsenous oxid.*—This variety is obtained by quickly cooling the vapor or by evaporation of the solution in water or hydrochloric acid. It crystallizes in regular octahedrons of specific gravity 3.689, and as the crystals form from the solution in hot hydrochloric acid, they phosphoresce in the dark. It is less soluble than the amorphous variety. It sublimes at 200° without melting, but melts under pressure.

2. *Prismatic arsenous oxid.*—This form is obtained by crystallizing from hot solution in potassium hydroxid, or by cooling the vapor slowly. It forms rhombic prisms of specific gravity 3.7.

3. *Amorphous or vitreous arsenic oxid.*—This is a colorless transparent vitreous mass obtained by condensing the vapor near the subliming temperature. It gradually becomes opaque and changes to

the octahedral form. The change is attended with the evolution of 5390 gram-heat-units and a slight decrease of specific gravity. It melts at 200°. At 600° the density is 198; at 1800°, 99.

Arsenous oxid dissolves slightly in water, readily in acids. The aqueous solution has a sweetish taste and a feebly acid reaction.

Chemical Properties.—Arsenous oxid unites with basic oxids to form arsenites, and in this respect arsenic is a non-metal. It also dissolves in acids forming salts and therefore has basic characters. It is, however, a very weak base, forming only a few compounds, among which are the halids and a sulfate, $As_2(SO_4)_3 + SO_3$. Nascent hydrogen converts arsenous oxid into arsin and carbon reduces it to arsenic. Hydrogen sulfid precipitates it from acid solutions as As_2S_3.

Physiological Properties.—Arsenous oxid is extremely poisonous. It has a twofold effect. In the first place it acts as an irritant, causing inflammation of the mucous membrane of the stomach, and in the second place it acts upon the nervous system. It causes nausea, thirst, trembling, delirium, and death. The antidote is freshly precipitated ferric hydroxid, which produces an insoluble ferric arsenite.

If arsenous oxid be taken in small doses and the dose increased from day to day, the system becomes accustomed to it, and large quantities may be taken with impunity. The effect is to produce for a time plumpness of form, softness of skin, whiteness of complexion, and improvement of breathing. It has therefore been used as a beautifier. It is sometimes fed to fattening hogs and wornout horses. When its use is abandoned, all the symptoms of arsenic poisoning appear.

Uses.—Arsenous oxid is used as a poison in the preparation of other arsenic compounds, in the manufacture of arsenical paints, anilin colors, and glass, and by taxidermists as a preservative.

ARSENIC OXID.

Formula As_2O_5. Molecular weight 230.

Preparation.—Arsenic oxid is not produced by direct oxidation of arsenic or arsenous oxid, but is obtained by bringing arsenic acid to a red heat: $2H_3AsO_4 = 3H_2O + As_2O_5$.

Properties.—Arsenic oxid is a white deliquescent solid of specific gravity 3.7. It dissolves in water to form arsenic acid and

at a temperature above a red heat decomposes into arsenous oxid and oxygen.

Arsenous and arsenic acids occur in three forms: ortho, di or pyro, and meta. They are analogous to the acids of phosphorus in formula and structure. They are as follows:

Orthoarsenous acid,	H_3AsO_3;	Orthoarsenic acid,	H_3AsO_4;
Diarsenous acid,	$H_4As_2O_5$;	Diarsenic acid,	$H_4As_2O_7$;
Metarsenous acid,	$HAsO_2$;	Metarsenic acid,	$HAsO_3$.

Arsenites.—The solution of As_2O_3 is feebly acid and probably contains both the ortho and meta arsenous acids. Arsenites are insoluble except those of the alkali metals. They are converted by heat into arsenates and are reduced by carbon to arsenic. Ammonium metarsenite, NH_4AsO_2, and ammonium diarsenite, $(NH_4)_4As_2O_5$, are obtained by dissolving arsenous oxid in ammonia.

Orthoarsenic Acid, H_3AsO_4, is formed by dissolving arsenic oxid in water, aqua regia, or chlorin water; or by oxidizing arsenous oxid with nitric acid. The concentrated solution is an oily liquid of specific gravity 2.0. · When cooled, it deposits rhombic crystals of composition $2H_3AsO_4,H_2O$, which at 100° lose the water of crystallization. The solution has an unpleasant, metallic taste, cauterizes the skin, and is poisonous, though less so than some other arsenic compounds.

Diarsenic Acid, $H_4As_2O_7$, is obtained by heating the ortho acid to 180°: $2H_3AsO_4 = H_2O + H_4As_2O_7$. It forms clear lustrous crystals which dissolve in water, passing back to the ortho acid.

Metarsenic Acid, $HAsO_3$, is obtained by heating the ortho or di acid to 200°. It is a white iridescent solid which dissolves in water to form the ortho acid. At a red heat it dissociates into arsenic oxid and water.

Arsenates.—Three classes of arsenates are formed corresponding to the three acids, and they may be normal, acid, or double salts. They are isomorphous with the phosphates. Hydrogen sulfid reduces arsenic acid and arsenates, precipitating from their solutions yellow arsenous sulfid, As_2S_3. The arsenates of the alkali and alkali-earth metals are soluble in water and the other neutral and basic arsenates are soluble in acids. Arsenates are generally obtained by

adding hydrogen disodium arsenate, HNa_2AsO_4, in molecular proportions to solutions of salts of various metals.   The di and meta arsenates when dissolved in water pass back into the ortho compounds.

Ammonium Arsenates.—The compounds, $H_2(NH_4)AsO_4$, $H(NH_4)_2AsO_4$, and $(NH_4)_3AsO_4$, are formed by the action of ammonia upon ortho-arsenic acid.

Chromates and **Molybdates** of arsenic are obtained by the action of chromic and molybdic oxids upon arsenic acid.

COMPOUNDS OF ARSENIC WITH SULFUR.

Arsenic unites directly to sulfur in three proportions:

Arsenic disulfid (Realgar), As_2S_2 $S=As—As=S$;
Arsenous sulfid (Orpiment), As_2S_3 $S=As—S—As=S$;
Arsenic sulfid, As_2S_5 $S=As—S—As=S$.
$$\underset{S}{\overset{\parallel}{}}\qquad\underset{S}{\overset{\parallel}{}}$$
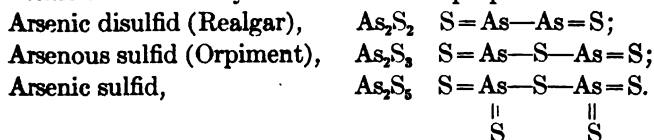
Arsenic Disulfid, As_2S_2, occurs native as *realgar* in ruby-red monoclinic prisms.   It may be prepared by melting sulfur with arsenic or arsenous oxid: $2As_2O_3 + 7S = 2As_2S_2 + 3SO_2$.   It is commercially prepared by heating together iron pyrites and arsenical pyrites: $2FeAsS + 2FeS_2 = FeS + As_2S_2$.

It is a red vitreous translucent solid of specific gravity 3.5.   It melts easily and sublimes unchanged, and burns in the air to arsenous and sulfurous oxids.   It is used in pyrotechny.   The Indian or Bengal fire is made with a mixture of 1 part arsenic disulfid with 12 parts of nitre and a little sulfur.   It gives an intensely white light.   Arsenic disulfid has been used also as a pigment and in tanning, being mixed with lime to remove the hair from the skins.

Arsenous Sulfid, As_2S_3, occurs native as *orpiment* in translucent yellow rhombic prisms of specific gravity 3.46.   It may be prepared by the action of hydrogen sulfid upon acid solutions of arsenic, or by fusing arsenous oxid with sulfur.   It is a lemon-yellow solid which melts easily and sublimes at 700°.   It is insoluble in water, but dissolves in alkalis and alkali carbonates, from which solutions it is precipitated by acids.   It burns readily to arsenous and sulfurous oxids.

Arsenic Sulfid, As_2S_5, may be obtained by fusing arsenous sulfid with a proper amount of sulfur, or by adding an acid to a solution of sodium thioarsenate:

$$2Na_3AsS_4 + 6HCl = 6NaCl + 3H_2S + As_2S_5.$$
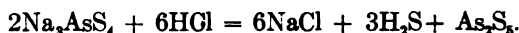
It is a yellow, easily fusible solid.

THIO ACIDS AND THIO SALTS OF ARSENIC.

When the sulfids of arsenic are acted upon by alkali sulfids, thio salts are obtained which are exactly analogous to the corresponding oxygen compounds:

$$Cl_2O_3 + 3K_2O = 2K_3ClO_3; \quad As_2S_3 + 3K_2S = 2K_3AsS_3.$$
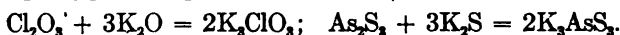
There are thioarsenites and thioarsenates of ammonium, chromium, molybdenum, and uranium.

No compound of arsenic with nitrogen is known, but *arsenous phosphid*, AsP, is precipitated as a brown powder when hydrogen sulfid is passed into phosphorus trichlorid.

ANTIMONY.

Symbol Sb. Atomic weight 120. Density 120. Molecular weight 240. Specific gravity 6.7. Valence III. and V. Melting-point 425°.

Occurrence.—Antimony occurs free in small quantities in various parts of the world, especially in Borneo. Its principal ore is *stibnite* or *gray antimony*, Sb_2S_3. Other native compounds are *antimony bloom* or *white antimony*, Sb_2O_3; *antimony ocher*, Sb_2O_4; *antimony blend* or *red antimony*, $Sb_2O_3,2Sb_2S_3$; and numerous double sulfids with copper, iron, lead, silver, nickel, etc.

History.—Antimony sulfid or *stibnite* has been known from the earliest times. It was called *kohl* by the Hebrews and Arabians, *stimmi* by Dioscorides, *stibium* by Pliny, and *antimonium* by Geber and Valentine. It was used as a pigment, notably for painting the eyebrows. The method of preparing the element was first described by Valentine.

Preparation.—Antimony is obtained from the sulfid in two ways:

1. By first roasting it in the air to produce the oxid and then reducing the oxid with carbon:

$$Sb_2S_3 + 9O = Sb_2O_3 + 3SO_2. \quad Sb_2O_3 + 3C = 3CO + Sb_2.$$
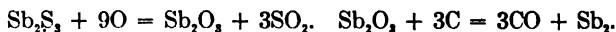
2. By heating it with iron: $Sb_2S_3 + 3Fe = 3FeS + 2Sb.$

The crude antimony thus obtained is refined by fusion with nitre, whereby the arsenic, sulfur, and lead are removed.

Physical Properties.—Antimony is a silver-white brittle solid with highly metallic lustre and specific gravity 6.7 to 6.8. It crystallizes in rhombohedrons which melt at 630° and distil at a white heat. As it crystallizes it expands so that it and its alloys make sharp castings.

Chemical Properties.—Antimony is not altered in the air, but when heated it takes fire and burns to antimonous oxid, Sb_2O_3. It unites directly to the halogens, inflaming spontaneously in chlorin and bromin. It is insoluble in water and dilute acids, but is attacked by strong acids, hydrochloric and sulfuric acids giving the chlorid and sulfate, and it is oxidized by nitric acid. All its soluble salts are poisonous, but less so than those of arsenic.

Antimony, like arsenic, is both a metal and a non-metal, but its metallic character is more marked. We have antimony salts and antimony acids with antimonites and antimonates. As usual it is more basic with the lower valence and more acidic with the higher valence.

Amorphous or **Explosive Antimony,** similar to amorphous arsenic, is said to be obtained by electrolysis of a solution of tartar emetic in antimony chlorid. It is a lustrous amorphous solid of specific gravity 5.78. It contains from 4 to 20 per cent of antimony chlorid and some occluded hydrogen. A slight blow or a scratch with a needle causes it to change to the common form with violence, and it explodes when heated to 200°.

Illustrations.—To show the combustion of antimony, direct a blow-pipe flame upon a fragment on charcoal. The antimony melts and burns, the oxid being deposited on the coal. If the melted globule be thrown upon a sheet of paper it breaks in many pieces, which run about over the paper, leaving fanciful streaks of the oxid.

Tests.—Antimony is detected as in Marsh's test for arsenic. The antimony spot is insoluble in sodium hypochlorite.

Alloys of Antimony.—Antimony forms numerous alloys, some of which are of commercial importance. Type metal contains about 20 per cent, stereotype metal 15 per cent, and Babbitt metal 13 per cent of antimony.

Uses of Antimony.—Antimony is used in the manufacture of tartar emetic and other medicinal preparations and in alloys as

above. Antimony black, obtained by the action of zinc upon antimonous chlorid, is used upon plaster casts to give them a metallic appearance.

ANTIMONY COMPOUNDS.

The compounds of antimony resemble those of arsenic, but are not quite so numerous. Its quality is mainly acidic, though it forms a few compounds and many alloys with the metals. It forms positive ions, antimonous $Sb^{...}$ and antimonyl $SbO^{.}$, and negative complex ions like those of arsenic. Some heats of formation are as follows:

$$(Sb,Cl_3) = 91{,}400 \text{ cal.} \qquad (Sb,Cl_5) = 104{,}900 \text{ cal.}$$
$$(Sb_2,O_3) = 166{,}000 \text{ cal.} \qquad (Sb_2,O_5) = 222{,}800 \text{ cal.}$$
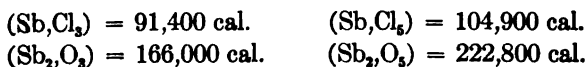
HYDROGEN ANTIMONID (STIBIN).

Formula H_3Sb. Molecular weight 123.

Preparation.—Only one compound of antimony with hydrogen, H_3Sb, is certainly known and it has not been obtained free from admixed hydrogen. It may be prepared—

1. By the action of nascent hydrogen, as when a solution of antimony chlorid is added to a mixture which is evolving hydrogen.

2. By the action of dilute sulfuric acid upon zinc antimonid:

$$Zn_3Sb_2 + 3H_2SO_4 = 3ZnSO_4 + 2H_3Sb.$$

3. By the action of water upon alkali antimonids:

$$2K_3Sb + 3H_2O = 3K_2O + 2H_3Sb.$$
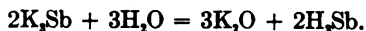
As prepared by any of these methods the gas is mixed with a large proportion of hydrogen.

Physical Properties.—Stibin is exactly analogous to arsin and closely resembles it in properties. It is a colorless poisonous gas with disagreeable odor and taste. It dissolves in one fourth its volume of water and gradually decomposes in the solution. At low temperatures it becomes a liquid which boils at $-18°$ and solidifies at $-102°$.

Chemical Properties.—Hydrogen antimonid is unstable, decomposing slowly in the cold and rapidly when heated. It burns in the air with a gray flame to water and antimonous oxid. If a cold plate be held in the flame a spot of antimony is formed which may be distinguished from the arsenic spot by its lack of luster and its insolubility in sodium hypochlorite. It is decomposed by acids,

alkalies, and the halogens, and by sulfur and hydrogen sulfid in sunlight. From silver nitrate it precipitates silver antimonid, Ag₃Sb, differing from arsenic, which separates metallic silver.

Illustrations.—The formation and properties of hydrogen antimonid may be shown with the Marsh arsenic apparatus. When the hydrogen is coming off freely add a hydrochloric-acid solution of antimonous oxid. Light the jet of escaping gases, note the color of the flame, make spot on cold plate and compare with the arsenic spot, heat the tube and note that the antimony is deposited on both sides of the heated point.

Antimonids.—Antimony does not form very definite compounds with the metals. It rather makes alloys, generally mixing in all proportions.

Stibonium Compounds.—Hydrogen antimonid is scarcely alkaline. Its solution in water may contain *stibonium hydroxid*, SbH_4OH, but this compound has not been isolated, nor are any compounds known corresponding to the ammonia and ammonium derivatives in which hydrogen remains united to antimony. There are, however, many stibin and stibonium derivatives in which all the hydrogen atoms have been replaced by organic radicals, negative elements, and acid radicals. Examples are, trimethyl stibin, $(CH_3)_3Sb'''$, and tetramethyl stibonium chlorid, $(CH_3)_4Sb^VCl$.

COMPOUNDS OF ANTIMONY WITH THE HALOGENS.

The halids of antimony are formed in general by the action of the halogens or haloid acids upon antimony or soluble antimony compounds. Both the tri and penta halids are formed as follows:

| Antimonous halids, | SbF_3 | $SbCl_3$ | $SbBr_3$ | SbI_3. |
| Antimonic halids, | SbF_5 | $SbCl_5$ | | SbI_5. |

Antimonous Fluorid, SbF_3, is a white deliquescent solid which crystallizes in rhombic pyramids. It dissolves in water to antimonous oxyfluorid, SbOF.

Antimonic Fluorid, SbF_5, is a gum-like solid which forms double compounds with alkali fluorids such as SbF_5,KF and $SbOF_3,NaF$.

Antimonous Chlorid, $SbCl_3$, is a soft, colorless, deliquescent, crystalline solid, known as *butter of antimony*. It melts at 73° to an oily liquid and boils at 223°, yielding a vapor of density 112.8, indicating the formula $SbCl_3$. It dissolves in a very small quantity of water to a clear liquid of specific gravity 1.35, known as *liquid*

butter of antimony. With more water it is decomposed, yielding a number of oxychlorids, the simplest of which is SbOCl. This mixture of oxychlorids is known as *powder of Algaroth,* because it was much used in the sixteenth century by the Veronese physician Algarotus.

Antimonic Chlorid, $SbCl_5$, is a colorless fuming bad-smelling liquid which solidifies when cooled and melts at $-6°$. It dissociates when heated, but distils in vacuo at $79°$ unchanged. With little water it dissolves to a clear liquid which, evaporated over sulfuric acid, yields crystals of $SbCl_5,4H_2O$. With more water several oxychlorids are formed.

Antimonous Bromid, $SbBr_3$, crystallizes in needles or octahedrons, melts at $94°$ and boils at $270°$. Dissolved in water, it forms several oxybromids, of which the simplest is SbOBr.

Antimonous Iodid, SbI_3, ruby-red crystals formed by the direct union of the elements. Its solution in water contains *antimony oxyiodid,* SbOI.

Antimonic Iodid, SbI_5, is a brown solid which melts at $78°$.

OXIDS OF ANTIMONY.

There are three oxids of antimony with formulas as follows:

Antimonous oxid, Sb_2O_3 $O=Sb-O-Sb=O$;

Antimony tetroxid, Sb_2O_4 $O=Sb-Sb=O$ or $O=Sb-O-Sb{<}^O_O$;

Antimonic oxid, Sb_2O_5 ${^O_O}{>}Sb-O-Sb{<}^O_O$.

Antimonous Oxid, Sb_2O_3 or Sb_4O_6, occurs native in rhombic crystals as the mineral *valentinite.* It may be prepared by burning antimony in air or oxygen, or by oxidizing antimony with nitric acid.

Antimonous oxid is a white crystalline powder which melts at a red heat and sublimes, condensing in rhombic prisms near the heated portion of the tube and in regular octahedrons further on. It is isomorphous with arsenous oxid and hence chemists are disposed to give it the formula Sb_4O_6. It is very slightly soluble in water to a neutral solution. It is insoluble in nitric and sulfuric acids, but dissolves in hydrochloric acid, forming the trichlorid.

Antimony Salts.—Antimonous oxid is rather basic than acidic. It forms two series of salts, those of trivalent antimony, as *antimonous nitrate,* $Sb(NO_3)_3$, and those of the radical (SbO)′, left after

taking the hydroxyl from metantimonous acid, as *antimonyl nitrate*, $(SbO)NO_3$.

Antimony Tetroxid, Sb_2O_4, may be regarded as a radical $(SbO_2)_2'$, or as a mixed oxid of trivalent and pentavalent antimony, an antimonyl antimonate, $(Sb'''O)'Sb^VO_5$, or $O=Sb-O-Sb\underset{O}{\overset{O}{<}}$. It may be obtained by burning the trioxid or igniting the pentoxid. It is a white non-volatile powder, insoluble in water. Boiled with hydrogen potassium tartrate it gives tartar emetic, $K(SbO)(C_4H_4O_6)$, and metantimonic acid, $HSbO_3$.

Hypoantimonates.—There are a few salts called *hypoantimonates* which may be supposed to be derived from the hypothetical hydrate of antimony tetroxid, $Sb_2O_4,H_2O = H_2Sb_2O_5$.

Antimonic Oxid, Sb_2O_5, is obtained by heating antimonic acid to 275°. It is a yellow amorphous powder, of specific gravity 5.6, insoluble in water, soluble in hydrochloric acid. At 300° it gives up oxygen and becomes Sb_2O_4. It is feebly acidic, and never basic. No antimonic salts are known.

ACIDS OF ANTIMONY.

Antimonous Acid, H_3SbO_3, has not been isolated, though it may possibly exist in the aqueous solution of antimonous oxid. The *metantimonous acid*, $HSbO_2$, is obtained by the action of sodium carbonate upon antimonous chlorid:

$$3Na_2CO_3 + 2SbCl_3 + H_2O = 6NaCl + 3CO_2 + 2HSbO_2.$$

When this is dissolved in sodium hydroxid, sodium antimonite, $NaSbO_2$, is produced. But few, if any, other antimonites have been prepared.

Antimonic Acids.—There are three antimonic acids similar in formula and structure to the acids of phosphorus and arsenic. They are unstable and form unstable salts and are not formed by the union of water and antimonic oxid.

Orthoantimonic Acid, H_3SbO_4, is formed by the action of water upon antimonic chlorid, or by allowing metantimonic acid to remain for a long time in contact with water.

Di or **Pyro Antimonic Acid,** $H_4Sb_2O_7$, is formed by the action of hot water upon antimonic chlorid, or by the action of hydro-

chloric acid upon diantimonates.   It is a white powder insoluble in water.

Metantimonic Acid, $HSbO_3$, is obtained by heating the ortho or di acid, or by the action of nitric acid upon antimony or antimonic oxid or antimonates.   It is a white powder, slightly soluble in water and acids.   It is a weak monobasic acid yielding mostly insoluble salts. '

Antimonates.—Antimonates are usually derived from the meta acid. There are a few diantimonates, but no orthoantimonates.

ANTIMONY WITH SULFUR, SELENIUM, AND TELLURIUM.

Antimonous Sulfid, Sb_2S_3, occurs in nature as the mineral *stibnite*, a dark-gray crystalline solid of metallic luster and specific gravity 4.7.   It is formed when antimony and sulfur are heated together, or when hydrogen sulfid is passed through solutions of the chlorid or tartrate.   When precipitated, it is a red amorphous powder which becomes crystalline when melted and cooled.   It oxidizes when heated in the air and dissolves in hydrochloric acid to form $SbCl_3$.   Red rubber is colored with antimony sulfid.

Antimony Sulfoxid, SbS_2O, has a red color and is called *antimony cinnabar*.   *Kermes mineral*, obtained by boiling antimony sulfid with sodium carbonate, is a mixture of Sb_2S_3 and Sb_2O_3.

Antimonic Sulfid, Sb_2S_5, is an orange-red powder obtained by treating acid solutions of antimonic acid with hydrochloric acid, or by treating sodium thioantimonate with HCl.   When heated it separates into Sb_2S_3 and S.

Thio Acids and Salts.—Both of the sulfids of antimony give rise to thio salts which may be ortho, di, or meta. ₁ An example is *Schlippe's salt, sodium thiantimonate,* Na_3SbS_4.

Antimonous Selenid, Sb_2Se_3, is a metallic-looking gray crystalline mass obtained by melting the elements together.

Antimonic Selenid, Sb_2Se_5, is precipitated as a brown powder from solutions of sodium selenantimonate by dilute sulfuric acid.

Seleno-antimonates.—There are a few salts which are derivatives of the hypothetical seleno-antimonic acid, H_3SbSe_4.   An example is sodium selenantimonate, Na_3SbSe_4, orange-red, transparent tetrahedrons isomorphous with sodium thioantimonate.

Antimonous Tellurid, Sb_2Te_3, is a tin-white solid obtained by fusing together antimony and tellurium.

ANTIMONY WITH NITROGEN, PHOSPHORUS, AND ARSENIC.

Antimony forms no compound with nitrogen, only one with phosphorus and two with arsenic.

Antimony Phosphid, SbP, is a tin-white solid obtained by adding phosphorus to melted antimony.

Antimonous Arsenid, Sb_2As_3, occurs native as the mineral *allemontite.*

ERBIUM.

Symbol Er.   Atomic weight 166.   Valence III.

Occurrence.—Erbium occurs along with a number of other rare elements in the mineral *gadolinite* from Sweden.

History.—Erbium was recognized as an element early in the nineteenth century, and it was carefully studied from 1860 to 1878. Because of its rarity and the difficulty of separating its compounds from those of the elements with which it is associated its chemistry is not very well made out.   The name is from Ytterby, a town in Sweden.

Preparation.—Erbium has not been obtained free. Its compounds are mostly prepared from the oxid which is obtained from gadolinite.

Halids of Erbium.—The fluorid, chlorid, bromid, and iodid have been described.   They are deliquescent, rose-colored salts.

Erbium Oxid, Er_2O_3, is a white powder obtained by heating the nitrate or oxalate.   It forms neutral and basic salts, and gives a continuous spectrum with bright bands.

Erbium Salts.—Erbium salts are obtained by dissolving the oxid in acids.   They are rose-colored and have a sweetish taste.   The more common ones are the sulfate, nitrate, phosphate, bromate, chlorate, iodate, carbonate, selenate, etc.

BISMUTH.

Symbol Bi.   Atomic weight 208.5.   Specific gravity 9.823.   Valence III and V.   Melting-point 270°.

Occurrence.—Bismuth usually occurs free.   It is also found in small quantities combined or associated with tellurium, copper, lead, and silver.   The principal native compounds are *bismuth ocher,* Bi_2O_3, and *bismuth glance,* Bi_2S_3.   The supply comes mainly from Saxony, near Schneeberg.

History.—Up to recent times bismuth was called *marcasite.* It was first described by Basil Valentine; it is mentioned by Paracelsus and Agricola; was first accurately studied by Bergmann. The English name is from the German *Wismuth.*

Preparation.—Bismuth is usually obtained from the native metal or the ores with which it is associated. The ores are heated in inclined iron pipes; the bismuth melts and runs away. The metal thus obtained may contain small quantites of iron, copper, lead, silver, antimony, tin, arsenic, and sulfur. It is purified by dissolving in nitric acid and precipitating it as basic nitrate by dilution with water: $Bi(NO_3)_3 + 2H_2O = 2HNO_3 + (BiO)NO_3,H_2O$. The dried basic nitrate is reduced by heating with carbon.

Physical Properties.—Bismuth is a brittle pinkish-white solid with metallic luster and specific gravity 9.823 at 12°. It melts at 270° and volatilizes in the electric arc. On cooling from fusion it expands and crystallizes in obtuse rhombohedrons which look like cubes as the angles are nearly 90°. Its specific heat is 0.0288.

Chemical Properties.—Bismuth tarnishes in moist air, becoming iridescent, and when heated burns to Bi_2O_3. It is insoluble in water and cold hydrochloric and sulfuric acids. It dissolves in nitric acid and hot sulfuric acid, forming with the first bismuth nitrate, $Bi(NO_3)_3$, and with the second the basic sulfate, $(BiO)_2SO_4$. Water decomposes bismuth solutions, precipitating insoluble basic salts.

Tests.—Bismuth is recognized by its color, appearance, and crystalline form. Salts of bismuth give white basic precipitates when diluted with water, and give black precipitates with hydrogen sulfid.

Uses.—Bismuth is used in the preparation of various medicines and cosmetics and in numerous alloys.

Alloys of Bismuth.—Bismuth forms with a number of metals alloys which melt at low temperatures and are called *fusible metals.* By using proper proportions an alloy can be had which will fuse at a given temperature. Wood's fusible metal has 4 parts bismuth, 2 parts lead, 1 part tin, and 1 part cadmium, and melts at 61°. Rose's fusible metal, which melts at 94°, has 2 parts bismuth, 1 part lead, and 1 part tin.

Fusible metal is used for stereotyping, for copying wood-cuts, for solder, for safety plugs for boilers, and for tempering steel.

BISMUTH COMPOUNDS.

Bismuth is scarcely negative and its one or two acids are unstable. As a positive it is not active and its compounds are not

numerous. It unites with the negative elements, but only alloys with the metals. The colorless trivalent ion Bi··· is weakly basic. Other ions are scarcely known, though there are basic compounds containing the radicals (BiO)' and (BiHO)''.

HALIDS OF BISMUTH.

No pentahalid of bismuth is known. The trihalids are formed by direct union or by dissolving bismuthous oxid in the strong haloid acids. They are as follows:

Bismuth fluorid, BiF_3, gray, heavy crystalline solid.
Bismuth chlorid, $BiCl_3$, white deliquescent crystals.
Bismuth bromid, $BiBr_3$, golden-yellow deliquescent crystals.
Bismuth iodid, BiI_3, dark-gray lustrous crystals.
With water these compounds form basic hydroxyhalids or oxyhalids:

$$BiCl_3 + 2H_2O = 2HCl + Bi(OH)_2Cl.$$
$$BiCl_3 + H_2O = 2HCl + BiOCl.$$
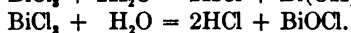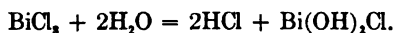
The halids of bismuth form double salts with other halids.

OXIDS OF BISMUTH.

Bismuth forms oxids corresponding to those of nitrogen, except that it does not act with valence I. These oxids are all basic, only the pentoxid possessing any acid properties at all. The trioxid is the most stable, and all the others when heated in the air are converted into it. The names and formulas are:

Bismuth dioxid, Bi_2O_2. Bismuthous oxid (Bismuth trioxid), Bi_2O_3.
Bismuth tetroxid, Bi_2O_4. Bismuthic oxid (Bismuth pentoxid), Bi_2O_5.

Bismuth Dioxid, Bi_2O_2, is a black crystalline powder obtained by heating bismuth in the air almost to fusion. It burns readily to the trioxid.

Bismuth Trioxid, Bi_2O_3, is formed by burning bismuth in air or oxygen, or by heating the hydroxids, the carbonate, or the basic nitrate. It is a yellow powder of specific gravity 8.2. It is insoluble in water, but dissolves in acids to form salts which upon addition of water are precipitated as basic salts.

Bismuth Tetroxid, Bi_2O_4 or $(BiO)BiO_2$, is a dark-brown powder formed by heating the trioxid with potassium hypochlorite and drying at 180°.

Bismuth Pentoxid, Bi_2O_5, is obtained by heating bismuthic acid, or by passing chlorin through a hot potash solution containing suspended bismuth. It is an unstable red powder, easily converted into the lower oxids by heat. When acted on by acids it forms salts of trivalent bismuth.

HYDRATES OF BISMUTH.

Bismuth dioxid forms no hydrate.

Bismuth trioxid does not unite directly to water, but three hydrates may be prepared with formulas as follows:

$$Bi_2O_3, 3H_2O = 2Bi(OH)_3, \qquad Bi_2O_3, 2H_2O = Bi_2O(OH)_4,$$
$$Bi_2O_3, H_2O = 2BiO(OH).$$
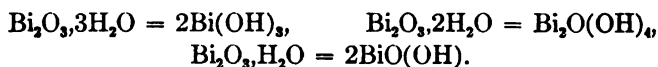
These hydrates have no acid properties, but are decidedly basic, acting with acids to form bismuthous and bismuthyl salts. The first, or orthobismuthous hydroxid, is formed by the action of strong ammonia upon a bismuth salt:

$$2Bi(NO_3)_3 + 6NH_4OH = 6NH_4NO_3 + 2Bi(OH)_3.$$
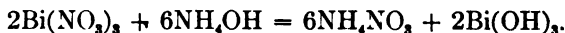
By heating the orthohydroxid the other two are formed.

Bismuth tetroxid unites to the moisture of the air to form the two hydrates, Bi_2O_4, H_2O and $Bi_2O_4, 2H_2O$. These act with acids in the same manner as the trioxid.

Bismuth pentoxid unites to water to form the hydrate Bi_2O_5, H_2O = $2HBiO_3$. This must be regarded as *bismuthic acid.* It is unstable, however, and almost if not quite devoid of acid characters. It yields no salts, and when acted upon by acids gives salts of trivalent bismuth. The di and tri hydrated compounds have not been isolated, but the dibismuthic acid, $H_4Bi_2O_7$, has been prepared.

SALTS OF BISMUTH.

In forming salts, bismuth is always trivalent. Besides the neutral compounds there are various basic salts in which a portion of the oxygen or hydroxyl remains attached to the bismuth atom.

Bismuth Sulfate, $Bi_2(SO_4)_3$, is a white amorphous solid obtained by dissolving bismuth or its trioxid in sulfuric acid. With water it forms the basic salt, $Bi(OH)_2SO_4$, which when heated becomes *bismuthyl sulfate,* $(BiO)_2SO_4$.

Bismuth Nitrate, $Bi(NO_3)_3, 3H_2O$, is obtained in triclinic prisms by dissolving bismuth in nitric acid.

Basic Bismuth Nitrate, $Bi(OH)_2NO_3$ or $BiONO_3$, commonly known as *bismuth sub-nitrate,* is precipitated when solutions of bismuth nitrate are diluted with water. It is a soft white powder which is finely crystalline. It is much used as a cosmetic, as a soothing application to abraded skin, and as a medicine, especially in cholera and diarrhea. It is also used in the manufacture of glass and porcelain.

Bismuth Orthophosphate, $BiPO_4$, and **Bismuth Pyrophosphate,** $Bi_4(P_2O_7)_3$, are formed when bismuth nitrate is acted upon by the corresponding acid of phosphorus.

Other bismuth salts are the the arsenates, chromates, carbonates, silicates, bromates, chlorates, vanadates, molybdates, etc.

BISMUTH WITH SULFUR, SELENIUM, AND TELLURIUM.

Compounds of bismuth with the sulfoids are formed by direct union of the elements. A few are given:

Bismuth disulfid, Bi_2S_2, gray needle-shaped crystals.
Bismuth trisulfid, Bi_2S_3, occurs native as the mineral bismuthite.
Bismuth thiochlorid, $BiSCl$, white needles insoluble in water and HCl.
Bismuth selenid, Bi_2Se_3, lustrous, brilliant crystals.
Bismuth tellurid, Bi_2Te_3, occurs native as the mineral tetradymite.

BISMUTH AND THE NITROIDS.

Bismuth does not form very definite compounds with the elements of the group to which it belongs. It does not combine with nitrogen and forms imperfect alloys with arsenic and antimony. Hydrogen phosphid and hydrogen arsenid both throw down black precipitates from bismuth solutions which are supposed to be *bismuth phosphid,* BiP, and *bismuth arsenid,* BiAs.

CHAPTER XXVII.

GROUP V A. THE VANADOIDS. VANADIUM GROUP.

Vanadium 51.2. Columbium 94. Praseodymium 140.5. Neodymium 143.6. Tantalum 183.

THE members of this group are all rare elements, vanadium being most abundant. They bear close resemblances to one another and to the nitroids, particularly to phosphorus and arsenic. They are more basic than the nitroids and do not form compounds with hydrogen, but the higher oxids form acids. They are allied to chromium, iron, and tungsten and are often found associated with them in nature. As in the nitroids, the valence is not very well defined.

VANADIUM.

Symbol V. Atomic weight 51.2. Valence I, III, V.

Occurrence.—Vanadium, though a rare element, is widely distributed in small quantities. It is often associated with other metals, particularly iron, lead, nickel, cobalt, and copper. The slag from the iron furnace sometimes contains 1 per cent of it. The spectroscope shows it to exist in the sun. The principal native compounds are *vanadinite*, $3Pb_3(VO_4)_2,PbCl_2$; *dechenite*, $(PbZn)(VO_4)_2$; *pucherite*, $BiVO_4$; and *mottramite*, $(PbCu)_3(VO_4)_2,2(PbCu)(OH)_2$.

History.—In 1801 Del Rio suggested the existence of a new metal in a lead ore from Mexico. In 1830 Woehler showed that this ore was a lead vanadate. In the same year Sepström found the new metal in iron ore from Taberg, Sweden, and called it *vanadium* from *Vanadis*, the Scandinavian name of the goddess Freia. The element was carefully studied by Berzelius in 1831, and its properties were more correctly ascertained by Roscoe in 1867.

Preparation.—Vanadium is obtained by reducing the dichlorid in a current of hydrogen. The operation is difficult, since vanadium so readily oxidizes, and every trace of moisture must be removed from the hydrogen.

Properties.—Vanadium is a gray powder of metallic luster and specific gravity 5.5. It is insoluble in water and cold acids, but makes a greenish-yellow solution in hot sulfuric acid. It unites directly to nitrogen and the halogens, and forms an alloy with platinum. Its valence is I, III, and V, and apparently II and IV. When heated with a full supply of air it burns to V_2O_5.

VANADIUM COMPOUNDS.

Space does not permit a detailed description of the numerous and complicated compounds of vanadium. The simpler compounds have formulas and chemical characteristics very like the corresponding compounds of nitrogen, phosphorus, and arsenic.

Halids and Oxyhalids of Vanadium.—The halids of vanadium are obtained by reducing the oxyhalids, or by the action of the halogen upon vanadium nitrid. The oxyhalids are obtained by the action of the halogens upon the oxids.

No fluorid nor oxyfluorid of vanadium is known, but there is a series of compounds called *fluoxyvanadates*, of which *potassium fluoxyvanadate* is an example, $3HKF_2,2VOF_3$:

$$\begin{matrix} H-F=F \\ H-F=F \\ H-F=F \end{matrix} \Big\rangle V <^O_O> V \begin{matrix} F=F-K \\ F=F-K \\ F=F-K \end{matrix}$$
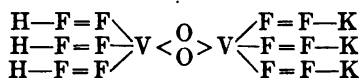
Vanadium dichlorid, VCl_2 or V_2Cl_4, apple-green, hexagonal crystals.

Vanadium trichlorid, VCl_3 or V_2Cl_6, peach-blossom-colored crystals.

Vanadium tetrachlorid, VCl_4, brownish-red fuming liquid, boils at 154°.

Divanadyl chlorid, V_2O_2Cl, yellow crystals.

Vanadyl chlorid, $VOCl$, flocculent brown powder.

Vanadyl dichlorid, $VOCl_2$, deliquescent green crystals.

Vanadyl trichlorid, $VOCl_3$, yellow liquid, boils at 127°.

Vanadium tribromid, VBr_3, unstable deliquescent black powder.

Vanadyl dibromid, $VOBr_2$, brown deliquescent powder.

Vanadyl tribomid, $VOBr_3$, red hygroscopic liquid, boils at 130°.

No iodin compounds of vanadium are known.

Oxids of Vanadium.—Vanadium forms five oxids corresponding to the oxids of nitrogen:

$$V_2O \qquad V_2O_2 \qquad V_2O_3 \qquad V_2O_4 \qquad V_2O_5$$
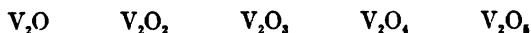
All these oxids are basic, and the last two are also acidic. They are formed in succession by the gradual oxidation of vanadium.

Vanadium Monoxid, V_2O, is a brown powder formed by long exposure of vanadium to the air.

Vanadium Dioxid, or **Hypovanadous Oxid**, V_2O_2, is obtained by reducing the higher oxids by potassium. It is a gray solid of specific gravity 3.64.

Vanadium Trioxid, or **Vanadous Oxid**, V_2O_3, is a black powder of specific gravity 4.7, obtained by heating the pentoxid in hydrogen. It oxidizes readily to the tetroxid, and gives, with chlorin, $VOCl_3$.

Vanadium Tetroxid, or **Hypovanadic Oxid**, V_2O_4, is a blue lustrous crystalline powder, obtained by oxidizing the trioxid or reducing the pentoxid.

Vanadium Pentoxid, **Vanadic Oxid**, V_2O_5, is prepared by oxidizing vanadium or the lower oxids, or by decomposing vanadyl trichlorid with water. It crystallizes in reddish-yellow rhombic prisms of specific gravity 3.35. It is soluble in strong acids and almost insoluble in water.

Hydroxids and Salts of Vanadium.—The oxids of vanadium have small affinity for water, so that the hydroxids are not well defined. The oxids dissolve in the acids to form salts which are mostly basic and of two series, one containing the radical (VO)''' and the other $(V_2O_2)^{IV}$. The first are called *vanadyl*, and the second *divanadyl* or *hypovanadic* salts. The following are examples:

Vanadyl sulfate, $(VO)_2(SO_4)_3$. Divanadyl hydroxid, $V_2O_2(OH)_4,5H_2O$.

Acids of Vanadium.—The two oxids V_2O_4 and V_2O_5 give rise to acids called *hypovanadic* and *vanadic* acids.

Hypovanadic Acid and Hypovanadates.—Vanadium tetroxid unites with water in various proportions. The salts called *hypovanadates* are mostly derived from the *hypovanadic acid*, $2V_2O_4,H_2O = H_2V_4O_9$. An example is *ammonium hypovanadate*, $(NH_4)_2V_4O_9$, a brown precipitate obtained by adding divanadyl sulfate to ammonia.

Vanadic Acid and Vanadates.—Orthovanadic acid has not been isolated. Metavanadic acid, HVO_3, is a brilliant yellow powder called *vanadium bronze*. It is formed by the action of hot sulfurous acid upon copper vanadate.

Pyro or Di Vanadic Acid, $H_4V_2O_7$, is a brown powder obtained by treating an acid vanadate with nitric acid.

In addition to the ortho, meta, and di vanadates, there are many polyvanadates, and also mixed vanadates containing arsenic, phosphorus, molybdenum, tungsten, silicon, or iodin.

Sulfids of Vanadium.—There are two sulfids of vanadium, both of which are acidic and form thio acids and thio salts.

Vanadium tetrasulfid, V_2S_4, is a black solid formed by the action of hydrogen sulfid upon heated vanadium tetroxid. Hypothiovanadates are formed by the action of alkali sulfids upon hypovanadic salts.

Vanadium pentasulfid, V_2S_5, is a black powder. *Thiovanadates* are formed by the action of hydrogen sulfid or alkaline sulfids upon vanadates.

Nitrids of Vanadium.—Two nitrids of vanadium have been prepared:

Vanadium nitrid, VN, is a gray metal-like powder obtained by the action of ammonia at a white heat upon an oxid of vanadium.

Vanadium dinitrid, VN_2, is a black powder obtained by the action of ammonia upon vanadyl trichlorid.

COLUMBIUM.

Symbol Čb. Atomic weight 94. Valence III, V.

Occurrence.—Columbium and tantalum are generally associated together in certain rare minerals, of which the following are the most important: *Pyrochlore*, a columbate of calcium, cerium, and other bases; *tantalite* and *columbite*, tantalo-columbates of iron and other bases; *yttrotantalite*, *fergusonite*, and *euxinite*, tantalo-columbates of yttrium and erbium; and *samarskite*, a tantalo-columbate of yttrium, uranium, and other bases.

In 1801 Hatchett found in a mineral from Connecticut an element which he called *columbium*. In 1844 Rose found in a mineral from Finland along with tantalum an element which he called *niobium*. The two elements proved to be the same. The latter name is generally used in Europe, the former in America.

Preparation.—Columbium is prepared by heating columbium trichlorid in a stream of dry hydrogen.

Properties.—Columbium is a steel-gray lustrous metal-like solid of specific gravity 7.06. It is insoluble in the acids except sulfuric acid. When heated in the air it burns to Cb_2O_5.

COLUMBIUM COMPOUNDS.

Halids and Oxyhalids of Columbium are similar to those of vanadium. Iodids of columbium are not known.

Oxids and Acids of Columbium.—There are three oxids, but only the highest one forms acids.

Columbium dioxid, Cb_2O_2, black, lustrous, regular crystals.

Columbium tetroxid, Cb_2O_4, black powder obtained by heating the pentoxid.

Columbium pentoxid, Cb_2O_5, white amorphous powder, specific gravity 4.53.

Metacolumbic acid, $HCbO_3$, is a white powder obtained by the decomposition of the oxychlorid or pentachlorid in moist air. It unites with varying quantities of water to form hydrates.

Columbates.—Numerous columbates and polycolumbates have been prepared, as well as compounds called fluocolumbates, an example of which is:

$$(NH_4)_2CbF_7,2CbOF_3,NH_4F.$$
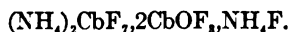
Columbium Oxysulfid, $CbOS_2$, is a black powder.

Columbium Nitrid, CbN, is a black powder obtained by heating columbium pentoxid in ammonia.

PRASEODYMIUM AND NEODYMIUM.

The element which was described by Mosander, in 1849, under the name *didymium* (*twin*, referring to its close relationship with lanthanum), has been separated by Welsbach by a long process of fractional crystallization of the ammonium didymium nitrate into two elements, which have been named *praseodymium* (praseo, green) and *neodymium* (neo, new). The salts of the former are green and those of the latter are rose-colored.

The atomic weight assigned to didymium was 142, and it fitted well into the periodic table, following columbium in group V. The atomic weights of the two constituents are $Pe = 140$ and $Nd = 143$. They are mostly trivalent and their place in the periodic table is a little uncertain. They are provisionally placed in groups V and VI, following cerium.

TANTALUM.

Symbol Ta.　Atomic weight 183.　Valence III, V.

Occurrence.—Tantalum occurs along with columbium in the rare minerals mentioned in connection with the history of that element.

History.—In the year 1801, Hatchett, of England, announced the discovery of a new metal in a columbite from Massachusetts, and called it *columbium*. In 1802, Ekeberg, in Sweden, found a new element in some yttrium minerals and called it *tantalum*, from Tantalus, because its investigation was troublesome. The two new elements were probably the same, though both the minerals used contained along with tantalum the element now called columbium.

Preparation.—Tantalum is separated from its native compounds by long and tedious processes. It may be obtained by heating in a crucible a mixture of potassium and potassium fluotantalate covered with potassium chlorid.

Properties.—Tantalum is a black powder insoluble in the acids except hydrofluoric. It unites directly to chlorin and burns in the air to Ta_2O_5. Its specific gravity is 10.78.

TANTALUM COMPOUNDS.

Tantalum Fluorid, TaF_5, is known only in solution. It gives rise to fluotantalates like $(NH_4)_2TaF_7$.

Tantalum Chlorid, $TaCl_5$, yellow crystals which melt at 211° and boil at 242°.

Tantalum Tetroxid, Ta_2O_4, a dark-gray powder, insoluble in acids, burns to Ta_2O_5.

Tantalum Pentoxid, or **Tantalic Oxid**, Ta_2O_5, white amorphous infusible powder, specific gravity 7.35 to 8.01, insoluble in water and acids.

Tantalic Acid, $HTaO_3$, is obtained by the action of water upon tantalum chlorid as a yellow, gelatinous mass.

Tantalates.—There are meta, di, and poly tantalates similar to the vanadates.

Tantalum Sulfid, Ta_2S_4, a gray granular solid.

Tantalum Nitrid, TaN, black, lustrous solid.

Tantalum Pentanitrid, Ta_2N_5, yellowish-red amorphous solid.

GROUP IV B. THE CARBOIDS. CARBON GROUP.

Carbon 12. Silicon 28. Germanium 72. Tin 119. Lead 207.

THIS group begins with the strongly acidic carbon and ends with the strongly basic lead.   As a whole the carboids are more metallic than the nitroids.   Carbon and silicon are negative and form acids, but do not form salts; germanium, tin, and lead form salts and also make weak acids when acting with the higher valences.   Only carbon and silicon form hydrogen compounds.   The valence of the group is IV, but germanium, tin, and lead act also as dyads.   They all form dioxids and, with the exception of silicon, monoxids.   They form ortho and meta hydrates, those of carbon and silicon being acids, while the others are basic with strong acids and acidic with strong bases.   All crystallize and tin and lead are malleable.

Some of the physical constants and formulas are as follows:

	Carbon.	Silicon.	Germanium.	Tin.	Lead.
Atomic weight.....	12	28	72	119	207
Specific gravity....	1.57 to 8.5	2.5	5.6	7.3	11.4
Melting-point......	....	1200°	900°	228°	325°
Specific heat.......	0.174	0.165	0.057	0.054	0.031
Oxids	CO, CO_2	SiO_2	GeO, GeO_2	SnO, SnO_2	PbO, PbO_2
Tetrachlorids	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
Ortho acids........	....	H_4SiO_4	H_4GeO_4	H_4SnO_4	H_4PbO_4
Meta acids.........	H_2CO_3	H_2SiO_3	H_2GeO_3	H_2SnO_3	H_2PbO_3
Hydroxids.........	....	....	GeH_2O_3	SnH_2O_3	PbH_2O_3

CARBON.

Symbol C.   Atomic weight 12.   Valence (II), IV.

Allotropic Forms of Carbon.—Carbon exists in three well-marked allotropic forms: (1) Diamond, (2) Graphite, and (3) Amorphous

390

Carbon.   These forms differ so much in physical properties that it is expedient to consider them separately.

DIAMOND.

Occurrence.—Diamonds occur in alluvial deposits and river gravels, in metamorphic regions, and are often associated with the micaceous rock called *itacolumite,* or *flexible sandstone.*   They were, no doubt, originally imbedded in the rock, were set free in the process of disintegration, and were carried along by the water and deposited with the detritus.   The chief localities are Purteal and Golconda in India, Brazil, South Africa, Australia, Borneo, the Ural Mountains, Georgia, North Carolina, and California.   The richest fields are in Brazil and South Africa.

History.—Diamond is mentioned by Greek writers three centuries before Christ under the name *adamas, unconquerable.*   This name was afterwards changed to *diamas,* from which we have the English word.   Diamond was described by Manilius in his *Astronomia* about b.c. 30.   It was first thought to be a species of rock crystal, but in 1694 its combustibility was shown by Averami and Targioni, who, at the suggestion of Duke Cosmo III of Tuscany, burned a diamond completely in the focus of a convex lens.   About 1790, Lavoisier and others showed that the product of its combustion is CO_2; and in 1814, Davy proved that only CO_2 is produced in its combustion.

Famous Diamonds.—The diamond is the most beautiful and most costly of precious stones.   Perfect specimens are rare and so generally small that the price increases in almost geometric proportion with the size.   The value is estimated by weight in terms of the *carat,* which is equal to 3.17 grains or 0.205 gram. The largest diamond of which we have record, mentioned by Taverni as in the possession of the Great Mogul, weighed before cutting 900 carats, and after cutting 279.6 carats.   The Pitt or Regent diamond weighs 136.25 carats and is of the first water.   It was sold to the regent Duke of Orleans for $675,000, and is now estimated to be worth $1,000,000.   It was placed by Napoleon in the hilt of the sword of state and was captured by the Prussians at Waterloo.   The Koh-i-noor (mountain of light), now in possession of King Edward VII, weighed 186 carats, but was reduced by cutting to 106.   The emperor of Austria has a yellow Tuscan diamond

which weighs 139.5 carats. The Orloff diamond in the Russian scepter weighs 194.25 carats. The Star of the South, found in Brazil, weighed 254.5 carats, but was reduced by cutting to 127.

The market price of diamonds fluctuates over a wide range. The average is about as follows: One-fourth carat, $30; one-half carat, $50; three-fourth carat, $100; one carat, $125; one and a half carat, $175; two carat, $250; three carat, $350; four carat, $500; five carat, $650.

Origin of the Diamond.—The origin of native diamonds is unknown. It is probable that they were derived from organic matter and that the crystallization of the carbon took place along with the metamorphism of the rocks.

Preparation.—Diamonds are crystallized carbon, and many attempts have been made to prepare them artificially. So far no stones of any value have been made. Microscopic diamond crystals have been obtained by dissolving carbon in molten cast iron and letting the iron cool under enormous pressure. On dissolving the iron away with nitric acid, very small diamond crystals are found in the residue. Microscopic diamonds are also formed when carbon-holding melted iron is poured in small quantity into cold water.

Properties.—Diamond occurs in three forms: crystalline, massive, and anthracitic. In the first form it is colorless and transparent and crystallizes in regular octahedrons and various modified forms
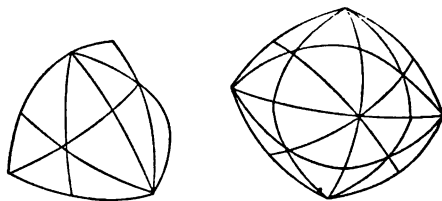
FIG. 65.—CRYSTALS OF DIAMOND.

of the isometric system. It refracts and decomposes light so powerfully that it is the most brilliant of gems. Its index of refraction is 2.43 higher than that of any other substance. The edges and faces are often curved, the cleavage is octahedral, and the fracture concoidal. The crystals are sometimes colored green, brown, or yellow, and may even be black. The specific gravity is 3.5 to 3.6. At 1000° it swells and becomes graphitic. It burns to CO_2, leaving 0.1 to 0.2 per cent of ash, mostly ferric and silicic oxids. It is a poor con-

ductor of electricity. Small imperfect crystals not fit for jewels are called *bort*.

Massive diamond occurs in black pebbles called *carbonado*. It has a specific gravity 3 to 3.25, and comes from Brazil.

Anthracitic diamond has the appearance of anthracite coal, but is as hard as the crystalline form. It has a specific gravity 1.66 and contains some hydrogen and oxygen.

Illustration.—The combustion of diamond (or graphite) may be shown as follows: Place a fragment on a piece of platinum foil connected to two copper wires, lower into a cylinder of oxygen and pass a rather strong electric current. The foil becomes red-hot and the diamond takes fire and burns in the oxygen.

Diamond-cutting.—Diamond is the hardest substance known. Indeed, it is difficult to conceive of its extreme hardness. Diamonds are cut by pressing them upon a revolving metallic wheel whose surface is covered with a mixture of diamond dust and oil. The process is slow, requiring months and even years for the finishing of large stones.

Uses.—The colorless transparent diamond crystals are used almost exclusively for settings in jewelry. The smaller imperfect stones are used for cutting glass, for which purpose the curved edge of the natural crystal is required. Coarse and colored stones are used for pointing drills and in powder for cutting diamonds.

GRAPHITE.

Occurrence.—Graphite occurs rather abundantly in various parts of the world. It is associated with crystalline rocks and is probably a highly metamorphic coal. The principal localities are in Siberia, Ceylon, Norway, India, the Eureka graphite mines in California, and in other parts of the United States.

History.—Graphite was known to the ancients, but was not distinguished from molybdenum sulfid, Mo_2S, both being called *molybdena*, or *plumbago* (supposed to contain lead). It has long been used for making pencils, and hence its name, which is from the Greek word which means *to write*. In 1779 Scheele distinguished it from molybdenum sulfid and showed that it was converted into CO_2 by nitric acid.

Preparation.—Carbon crystallizes from solution in molten iron as graphite. The iron may be dissolved away and the crystals obtained.

Properties.—Graphite is a soft black unctuous solid of specific gravity 2 to 2.5. It occurs in foliated masses or in six-sided tabular crystals. It is a good conductor of heat and electricity. It burns with difficulty, melts at a very high temperature, and when mixed with clay forms one of the most refractory substances known. When heated with potassium chlorate and nitric acid, it is converted into *graphitic acid*, a yellow crystalline substance whose formula has not been determined. This is decomposed by heat, leaving a very finely divided graphite, the form which is used to cover the electrotype moulds.

Uses.—The most important general use of graphite is in the manufacture of lead-pencils. The graphite is powdered, washed free from grit, and mixed with finely divided clay and enough water to make a thick paste. This mixture is forced through holes the size of the pencil leads, and the graphite cylinders thus formed are cut into proper lengths and covered with cedar sticks. The hardness of the pencil is determined by the proportion of clay and the amount of pressure. Graphite mixed with clay is the material of crucibles used in many metallurgical operations. Finely divided graphite is used for polishing gunpowder and iron articles such as stoves, and for covering the moulds upon which electrotype plates are to be made; also as a lubricant for machinery where oil cannot be used.

AMORPHOUS CARBON.

Amorphous carbon is obtained by heating carbon compounds away from the air. The three principal sources and the forms derived from them are as follows:

1. Vegetable matters.   2. Animal matters.   3. Coal.
    a. Charcoal.   *a.* Boneblack.   *a.* Coke.
    b. Lampblack.   *b.* Ivoryblack.   *b.* Gas carbon.

Charcoal.—The purest charcoal is obtained by heating white sugar in a platinum dish and igniting it in a current of pure chlorin. As thus obtained, it is black, tasteless, odorless, conducts electricity well, and has a specific gravity 1.5. It is used in laboratories as a reducing agent.

Common charcoal is obtained by heating wood or other organic substances with a limited supply of air, or in closed vessels away from the air.

In the first case the wood is charred by its own partial combustion. It is piled in heaps and covered with brushwood and earth and lighted in the interior, the supply of air being so regulated that the heat is mainly produced by the combustion of the volatile matters, while the carbon remains.

In the second method the wood is inclosed in cylinders or retorts and the heat applied outside. In this case the volatile products may be collected and utilized. These are principally water, wood alcohol, pryoligneous acid, oils, and tar, which are condensed as liquids; and hydrogen, carbon monoxid, carbon dioxid, marsh-gas, and acetylene, which pass off as gases.

Charcoal varies in its physical properties with the kind of wood used and the temperature at which it is formed. When made at 300° it is a soft porous black solid which ignites at 380°. It has a specific gravity 0.1 to 0.2 when its pores are filled with air and 1.5 when they are filled with water. It therefore swims when first placed on water, but finally sinks. It absorbs gases with vigor, condensing them within its pores. At the ordinary temperature it absorbs 90 volumes of ammonia, 85 of hydrogen chlorid, 65 of sulfurous oxid, 55 of hydrogen sulfid, 35 of carbon dioxid, 9 of oxygen, 6 of nitrogen, and 1 of hydrogen. It also has the power of withdrawing substances from solution, either simply retaining them or decomposing them. In this respect it is most effective with coloring matters and alkaloids.

Charcoal is one of the most durable of substanecs. It is unchanged in the air and not attacked by the acids. Heated, it burns without smoke or flame. Charcoal made at a high temperature is hard and compact and must be heated to 700° before it ignites.

Illustrations.—To prepare charcoal place in a test-tube a dozen or more match-sticks, close with a cork through which passes a tube drawn to a small opening, support horizontal, and heat. Water comes off first, then gases which may be lighted, while tar-like matters collect in the cooler portion of the tube, or in a receiver.

To show the absorption of gases by charcoal pass a freshly ignited piece into a cylinder of ammonia-gas over mercury. The ammonia is rapidly absorbed and the mercury rises in the cylinder. If a piece of charcoal which has been long exposed to the air be immersed in hot water the gases are rapidly expelled and bubble out through the water.

To show the action of charcoal upon solutions, fill a filter with freshly ignited and powdered charcoal and pour upon it ink, wine, or solution

of anilin colors, potassium permanganate, or hydrogen sulfid. The hydrogen sulfid loses its odor and the colors are all discharged.
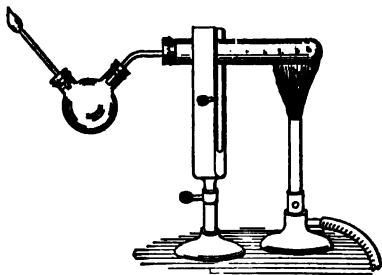
Fig. 66.

Lampblack.—When substances rich in carbon, like tar, resin, turpentine, and petroleum, are burned with an insufficient supply of air, they give off dense clouds of smoke which is largely composed of free carbon. The smoke is conducted into chambers hung with coarse cloths upon which the carbon collects as the fine powder called *lampblack*. Lampblack contains compounds of hydrogen and carbon, which may be removed by heating it in a stream of chlorin.

Lampblack is used mainly for making black paints and printers' inks. A very fine quality, obtained by letting the flame of oil-lamps play upon metallic plates, is used for making India ink and in calico-printing.

Illustration.—The formation of lampblack may be observed by burning some benzene in a watch-glass and holding over it a bell-glass. If a cold plate be held in a candle flame, or in the yellow Bunsen flame, it receives a black deposit of soot. The carbon is deposited because it is cooled by the plate below its burning temperature.

Animal charcoal or **Boneblack** is obtained by the dry distillation of bone in iron vessels. It contains the mineral matter of the bones and only about 10 per cent of carbon. It is highly active because the carbon is finely distributed through the porous mass of calcium phosphate. It is more efficient as an absorbent and chemical agent than wood charcoal, and is used as a decolorizer in the refining of sugar.

Ivoryblack is obtained by calcining ivory or teeth and has properties similar to those of boneblack.

Coal has been formed by the slow decomposition of vegetable matter in the presence of water and away from air.   It consists of free carbon mixed with various compounds of carbon, hydrogen, and oxygen, together with some mineral matter.   The specific gravity varies from 1.1 to 1.8. There are two general kinds, *hard* or *anthracite coal* and *soft* or *bituminous coal*, with many intermediate varieties.

Hard coal contains about 6 per cent of volatile matter and 90 per cent of carbon.   It burns with difficulty, scarcely yielding smoke or flame, but has a high heating power.

Soft coal contains about 30 per cent of volatile matter and 65 per cent of free carbon.   It is of two kinds, called *caking* and *non-caking* coal.   When the former burns, it melts and runs together, forming a cake, while the latter burns to ash without fusion.   Soft coal burns with flame and smoke and is used for ordinary fuel and in the manufacture of gas.   Coke is made from caking coal.

Cannel coal is a soft coal which contains 40 to 66 per cent of volatile matter and is used in the manufacture of burning and lubricating oils as well as for fuel.   It gets its name from the fact that small splinters can be lighted with a match and burn like a candle.

Brown coal or *Lignite* is compact and brown, sometimes black, and contains much volatile matter and a larger per cent of oxygen than the other coals.

Jet is a compact, black variety of lignite which takes a fine polish and is used in jewelry.

Peat is composed of vegetable matter very slightly altered.

Coke.—Coke is to coal what charcoal is to wood.   It is obtained by heating coal until the volatile matter is all driven off.   It is made in jug-shaped ovens having an opening above and one at the side below.   The oven is filled with coal and lighted and when well ignited the openings are closed and the heat converts the whole mass into coke.

Coke contains about 90 per cent of carbon, all the mineral matter of the coal, and small quantities of hydrogen, nitrogen, and oxygen. It is hard and lustrous, burns with difficulty, giving little flame and smoke, and has a high heating power.   It is largely used in the manufacture of iron and in processes which require a smokeless fuel.

Gas Carbon.—This form of coke is produced when coal is distilled in closed vessels, as in the manufacture of gas.   It is deposited

on the roof. and walls of the cylinders, and is a very pure carbon, almost free from mineral matter and hydrogen. It is of a steel-gray color, compact, and very hard, and conducts electricity well. It is used in batteries and as carbon rods for arc lights.

Composition of Coal and Wood.—The following table shows the composition of wood, peat, coke, charcoal, and the several kinds of coal. The figures vary greatly in different samples, and those are chosen which seem to represent an average.

	Carbon.	Oxygen.	Hydrogen.	Nitrogen.	Sulfur.	Ash.
Wood...............	50.0	40.0	6.0	1.6	....	2.4
Peat.................	60.0	31.0	5.8	1.0	....	2.2
Lignite..............	67.0	25.0	5.0	1.0	....	2.0
Bituminous coal	70.0	12.0	5.2	1.8	0.4	2.6
Cannel coal..........	80.0	8.0	5.6	2.1	1.5	2.8
Anthracite coal.......	90.0	3.0	3.3	0.8	1.0	1.9
Coke	92.0	2.0	0.3	0.4	0.1	5.2
Charcoal.............	85.6	3.8	2.9	1.3	....	6.4

General Properties of Carbon.—In all its forms carbon is practically infusible and non-volatile. Except as diamond, it is always black or gray in color. At the ordinary temperature it is without chemical activity and remains unaltered indefinitely. It unites directly at moderate temperatures with very few elements. At red heat it combines with oxygen, sulfur, hydrogen, and nitrogen. In its compact form as diamond, graphite, and gas carbon it burns with great difficulty; as coke and anthracite coal it burns freely when well ignited; as charcoal it burns easily because of its porosity. Its heat of combustion is 97,000 calories. Its valence is four, though in a few cases it seems to act as a dyad. It is electro-negative and forms no salts. Its oxid and sulfid both form acids.

Carbon softens and is somewhat volatile at 3500° and under great pressure melts in the electric furnace. It is insoluble in water, acids, and alkalis, but dissolves in molten metals.

Carbids.—At the temperature of the electric furnace, carbon is made to combine with a number of the metals. The most important of these compounds is *calcium carbid*, CaC_2, now much used in the preparation of acetylene gas.

Uses.—Carbon finds various uses in the arts besides those already mentioned in connection with its allotropic forms. It is the princi-

pal constituent of all fuels and is the common reducing agent for separating the metals from their ores.

Illustrations.—Heat in a small tube a mixture of charcoal and arsenous oxid.   The reduced arsenic is deposited as a dark ring on the tube.

Sprinkle a little freshly ignited boneblack on a bit of phosphorus. The phosphorous takes fire because of the action of the condensed oxygen.

COMPOUNDS OF CARBON.

Carbon forms in the ordinary way a few compounds such as carbon dioxid, carbon disulfid, the carbids, and the carbonates. Besides these there is an immense number of compounds called *organic,* because many of the most important ones are found in the bodies of plants and animals.   They are composed of but few elements, mainly carbon, hydrogen, oxygen, and nitrogen, though nearly all the other elements may be introduced.   Some contain only carbon and hydrogen and are called *hydrocarbons.*   Others contain carbon, hydrogen, and oxygen and are divided into many classes such as alcohols, acids, ethers, etc.   Still others contain also nitrogen and are called *nitrogenous organic compounds.*   So numerous are these carbon compounds that they are usually treated in a separate work called *organic chemistry.*

COMPOUNDS OF CARBON WITH HYDROGEN.

Carbon forms with hydrogen a large number of compounds which fall into several series, the successive members of which differ by a constant quantity, CH_2.   The carbon atoms possess the property of linking themselves together in chains and circles and in this way the number of possible compounds is almost un-

limited.   Examples are methane, $H—C—H$; ethane, $H—C—C—H$;

propane, $H—C—C—C—H$;   butane, $H—C—C—C—C—H$,   etc.

There are four principal series, the first few members of which are as follows:

Marsh-gas Series.	Ethylene Series.	Acetylene Series.	Benzene Series.
Methane CH_4	Ethylene C_2H_4	Acetylene C_2H_2	Benezene C_6H_6
Ethane C_2H_6	Propylene C_3H_6	Allylene C_3H_4	Toluene C_7H_8
Propane C_3H_8	Butylene C_4H_8	Crotonylene C_4H_6	Xylene C_8H_{10}
Gen. Form. C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}	C_nH_{2n-6}

Only the first member of each of these series will be treated in this connection. They have structures as follows:

Methane $\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H.}$ Ethylene $\mathrm{H{-}\overset{\displaystyle H}{C}{=}\overset{\displaystyle H}{C}{-}H.}$ Acetylene $\mathrm{H{-}C{\equiv}C{-}H.}$

Benzene
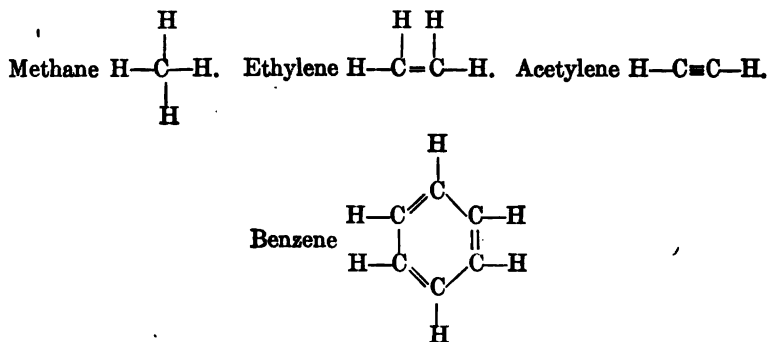
METHANE OR MARSH-GAS.

Formula CH_4. Molecular weight 16. Density 8.

Occurrence.—Methane is a product of the decomposition of vegetable matter under water. When the mud at the bottom of a stagnant, marshy pool is stirred, bubbles of gas arise which consist largely of methane, hence the name *marsh-gas*. It was produced in the formation of coal and is found confined under pressure in the coal-beds and in their vicinity. It forms an explosive mixture with the air and is the *fire-damp* of the miners. It is a large constituent of natural gas, coming from wells and petroleum springs. The holy fire at Baku on the Caspian Sea, which has existed from time immemorial, is burning methane.

Preparation.—Methane is always a product of the dry distillation of organic bodies, as well as of their slow decomposition under water. In the laboratory it may be obtained in the following ways:

1. By the action of water upon zinc methyl:

$$Zn(CH_3)_2 + 2H_2O = Zn(HO)_2 + 2CH_4.$$
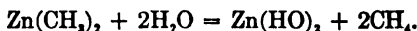
2. By passing a mixture of carbon disulfid and hydrogen sulfid over red-hot copper: $2H_2S + CS_2 + 8Cu = 4Cu_2S + CH_4.$

3. By heating an acetate with a strong alkali, as soda lime:

$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4.$$

To prepare methane by the last reaction, heat in an iron tube or copper flask a mixture of one part sodium acetate and four parts soda lime and collect the gas over water. Thus prepared it contains hydrogen and ethylene.

Physical Properties.—Methane is a gas, colorless, tasteless, and almost odorless, with specific gravity 0.55. Under the influence of pressure and cold, it becomes a liquid which boils at $-144°$. Its critical temperature and pressure are $-95°$ and 50 atmospheres. It dissolves slightly in water, one part to twenty, but is more soluble in alcohol.

Chemical Properties.—Methane is quite stable and is not attacked by acids, but is decomposed at a white heat. Its heat of formation is 21,800 calories. It burns readily with a pale-blue, faintly luminous flame to carbon dioxid and water. It makes explosive mixtures with two volumes of oxygen, ten of air, or one of chlorin. Mixed with chlorin, it remains unchanged in the dark, but in direct sunlight explodes with separation of carbon:

$$CH_4 + 4Cl = 4HCl + C.$$
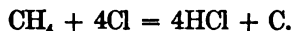
In diffused daylight the chlorin replaces the hydrogen atom by atom as follows:

$CH_4 + 2Cl = HCl + CH_3Cl$, methyl chlorid, a colorless gas.
$CH_4 + 4Cl = 2HCl + CH_2Cl_2$, methylene chlorid, a light liquid.
$CH_4 + 6Cl = 3HCl + CHCl_3$, chloroform, a light liquid.
$CH_4 + 8Cl = 4HCl + CCl_4$, carbon tetrachlorid, a colorless liquid.
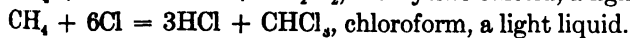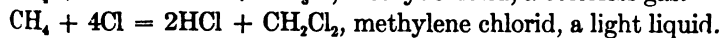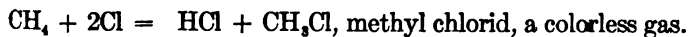
The radical CH_3 obtained by removing one H from methane is called *methyl*. It acts like a positive element and enters into an immense number of organic compounds. The second member of the series, ethane, C_2H_6, gives the similar radical, *ethyl*, C_2H_5; the third gives *propyl*, C_3H_7, etc.

The compounds belonging to the marsh-gas series, up to the one containing thirty carbon atoms, are nearly all contained in petroleum, and the higher members constitute the white solid called *paraffin*. They are therefore sometimes called *paraffins*, the word being from the Latin, and meaning *little affinity*.

Illustrations.—Mix methane with air, oxygen, or chlorin, and ignite. Bring a flame to the mouth of a jar of the gas, or ignite a jet. The gas prepared as usual will burn with a luminous flame. If it be passed through sulfuric acid the flame is nearly non-luminous.

<div align="center">

ETHYLENE.

</div>

<div align="center">

Formula C_2H_4. Molecular weight 28. Density 14.

</div>

Occurrence.—Ethylene occurs along with methane in gaseous exhalations from coal-beds, oil-springs, and wells, and in natural gas, and is a constituent of coal-gas.

Preparation.—Ethylene is formed—

1. By the destructive distillation of organic matters and coal.

2. By the action of alcoholic potash upon ethyl iodid, or of zinc-copper couple upon ethylene dibromid.

3. By dehydrating alcohol with phosphorus pentachlorid or sulfuric acid: $C_2H_6O - H_2O = C_2H_4$

To prepare ethylene by the last reaction, place in a flask a mixture of one part alcohol and six parts sulfuric acid, heat to boiling and add slowly through a funnel tube a mixture of equal parts of the alcohol and acid. The gas is purified by passing through sulfuric acid and potassium hydroxid, and collected over water.

Physical Properties.—Ethylene is a colorless gas with a pleasant, ethereal odor and a specific gravity 0.98. It dissolves in four volumes of water and in half its volume of ether or alcohol. When cooled under pressure it becomes liquid and solid; melts at $-169°$, and boils at $-105°$. Its critical temperature and pressure are $13°$ and 60 atmospheres.

Chemical Properties.—Ethylene burns with a brightly luminous flame, decomposing first into methane and acetylene, and finally yielding carbon dioxid and water. It is an unsaturated compound, the carbon atoms being doubly linked, and hence forms addition products. It unites directly to the halogens, the haloid acids, and other compounds, yielding derivatives of the marsh-gas series $\begin{smallmatrix}H\\H\end{smallmatrix}{>}C = C{<}\begin{smallmatrix}H\\H\end{smallmatrix} + Cl_2 = $ $\begin{smallmatrix}H\\H\\Cl\end{smallmatrix}{>}C{-}C{<}\begin{smallmatrix}H\\H\\Cl\end{smallmatrix}$. Its heat of formation is -3000 calories.

Illustrations.—Fill a jar with equal parts of ethylene and chlorin and ignite. The mixture burns with a greenish flame.

Invert a similar jar over water. The gases slowly unite and oily

drops of ethylene chlorid sink through the water. From this action it obtained the name *olefiant gas.*

Fill a flask with ethylene and add a few drops of bromin. The bromin is soon replaced by colorless ethylene bromid.

ACETYLENE.

Formula C_2H_2. Molecular weight 26. Density 13.

Occurrence.—Acetylene scarcely occurs free except as a constituent of natural gas and coal-gas. The illuminating power of these gases is largely due to acetylene and ethylene.

Preparation.—Acetylene may be prepared—

1. By direct union of carbon and hydrogen, as when the electric arc between carbon electrodes is surrounded with hydrogen.

2. By combustion of hydrocarbon gases with an insufficient supply of air, as when a Bunsen lamp burns at the base of the chimney.

3. By the action of alcoholic potash upon ethylene bromid:

$$C_2H_4Br_2 + 2KHO = 2KBr + 2H_2O + C_2H_2.$$
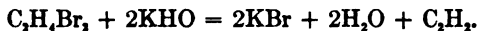
4. By the action of water upon carbids:

$$CaC_2 + 2H_2O = Ca(HO)_2 + C_2H_2.$$
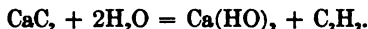
Acetylene is most conveniently prepared by the last method. The carbid is placed in a flask and the water is added drop by drop through a separatory funnel-tube. The gas is collected over water or burned from a jet.

Physical Properties.—Acetylene is a colorless gas with an unpleasant odor and specific gravity 0.92. It is poisonous, and even when dilute induces headache. It dissolves in its own volume of water and in one sixth its volume of alcohol. At 1° and under 48 atmospheres it becomes a colorless liquid which freezes by its own evaporation to a solid which melts at $-81°$. Its critical temperature and pressure are 37° and 68 atmospheres.

Chemical Properties.—Acetylene burns with a very smoky flame. With specially prepared burners it makes a very bright white light. It makes an explosive mixture with air or oxygen, unites energetically with chlorin and bromin, and with nascent hydrogen forms first ethylene, C_2H_4, and then ethane, C_2H_6. At a red heat three molecules unite to form benzene, C_6H_6, the fundamental compound of the aromatic series. The hydrogen atoms are replaceable by metals and some of the compounds thus formed are unstable and explosive, as for example the silver and copper acetylids. Its heat of formation is $-47,770$ calories.

Use.—Acetylene has recently come into use as an illuminant for private dwellings and business houses. The gas is generated in simple machines, is conducted through ordinary gas-pipes, and delivered through burners specially adapted. It is prepared from calcium carbid, which is made by heating together lime and coke in the electric furnace.
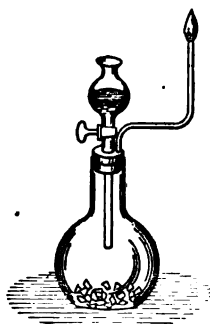
Illustration.—The acetylene light may be shown by igniting the gas flowing from a jet connected with the generator. The flame should be small.

Fig. 67.

BENZENE.

Formula C_6H_6. Molecular weight 78. Density 39.

Preparation.—Benzene is one of the products of the decomposition of many of its compounds. It is thus formed in the distillation of coal and petroleum. It is usually obtained from coal-tar by fractional distillation. The distillate coming over between 80° and 85° is mainly benzene. Pure benzene is obtained by distilling a mixture of benzoic acid and calcium oxid.

Physical Properties.—Benzene is a colorless, volatile, highly refractive liquid with a pleasant ethereal odor and a specific gravity 0.88. It dissolves in alcohol, ether, acetic acid, and chloroform, but scarcely in water. It dissolves sulfur, phosphorus, iodin, fats, resins, oils, and alkaloids. It crystallizes in trimetric pyramids. It solidifies at 0°, melts at 6°, and boils at 80.5°.

Chemical Properties.—Benzene may be lighted with a match and burns with a smoky flame. Its heat of formation is −12,510 calories, and its heat of combustion is 776,000 calories. It is easily acted upon by chemical agents, the hydrogen atoms being replaced by various elements and radicals, and giving rise to the almost innumerable compounds belonging to the *benzene* or *aromatic series*.

ILLUMINATING-GAS.

History.—In 1726, Stephen Hales obtained an inflammable gas from coal. The first practical use of it was made by William Murdoch, a Scotchman of Rudruth, in Cornwall. He lighted his

residence, and in 1798 he lighted a factory at Soho. ·In 1805 it was used in a large cotton-mill at Manchester. London was first lighted with gas in 1812, and Paris in 1815.

Manufacture of Coal-gas.—Coal-gas is prepared by the destructive distillation of coal. The products of the distillation fall into four classes:

1. Coal-gas, a mixture of many hydrocarbons.

2. Coal-tar, an oily tar-like liquid, also mainly composed of hydrocarbons.

3. Ammoniacal liquor, or gas-water, containing ammonia and ammonium compounds in solution.

4. Gas-carbon and coke which remain in the retorts. These have already been described.

Soft coal is heated to about 1100° in fire-clay or iron retorts. The products of the distillation are carried upward through a large pipe which turns downward and dips beneath water in a horizontal cylinder called the *hydraulic main*, in which are collected the tar and heavier liquids. The residual gases are passed through a series of vertical tubes called *condensers*, each opening below in a water vessel. In these more of the condensible and soluble gases are retained. The gas then passes through two towers, called *scrubbers*, filled with coke, over which plays a fine spray of water. In these are removed most of the hydrogen sulfid and ammonia. The gas is still further purified by passing through chambers containing slaked lime or ferric hydrate to free it as completely as possible from hydrogen sulfid and carbon disulfid, which in burning vitiate the air with sulfurous oxid, and from carbon dioxid, which as a diluent diminishes the illuminating power of the gas.

Composition of Coal-gas.—Coal-gas is a mixture of many substances in proportions which depend upon the nature of the coal from which it is made. The constituents may be classified into *luminants*, *diluents*, and *impurities*. These are present in average proportions about as follows:

1. *Luminants*, hydrocarbons rich in carbon which give a brilliant light and burn with a smoky flame unless diluted. These are mainly acetylene, C_2H_2, ethylene, C_2H_4, propylene, C_3H_6, and benzene, C_6H_6, together about 6 per cent.

2. *Diluents*, combustible gases which give but little light, yet help to consume the heavier luminants. Such are hydrogen, 46 per cent, methane, 40 per cent, and carbon monoxid, 4 per cent, in all about 90 per cent.

3. *Impurities* which are not removed in the purifying process and which are injurious to the gas, such as nitrogen, carbon dioxid, and hydrogen sulfid, about 4 per cent.

Illuminating Power of Gas.—The illuminating power of gas is determined by comparison with standard candles. A gas-flame burning 5 cubic feet of gas an hour is compared with the flame of a candle burning 120 grains (7.79 grams) of sperm an hour. Ordinary gas has a power of 13 to 16 candles, while gas made from cannel coal may run as high as 35 candles.

Coal-tar.—Coal-tar is a thick, black, oily, bad-smelling liquid. It is a very complex mixture rich in hydrocarbons of the benzene series, which may be separated by fractional distillation. The principal constituents are benzene, toluene, xylene, naphthalene, anthracene, carbolic acid, etc. The residue is a black pitch which is used as a varnish for iron articles, for covering roofing paper, and for making asphalt pavements.

Ammoniacal Liquor.—The water which comes from the hydraulic main and the condensers contains large quantities of ammonia and ammonium salts. It is the chief source of commercial ammonia.

Wood-gas.—Where wood is abundant it may be used as a source of illuminating-gas. The process of manufacture and purification is similar to that used for coal-gas. Wood-gas is rich in heavy hydrocarbons and carbon monoxid and has a high illuminating power. It is free from hydrogen sulfid. The liquid products of the distillation are acetic acid, methyl alcohol, acetone, creosote, and wood-tar. Wood is more often distilled for these liquids than for the gas.

Water-gas.—The so-called water-gas consists essentially of hydrogen and carbon monoxid obtained by passing steam over incandescent carbon:

$$C + H_2O = H_2 + CO.$$
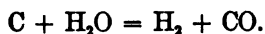
The luminosity of this mixture is increased by introducing a small amount of heavy hydrocarbons obtained from gasoline or naphtha.

CH_4 **Natural Gas.**—Natural gas comes from the earth in large quantities, particularly from deep borings, and is much used for fuel and light. It is found in the vicinity of coal-beds and in oil regions, and has no doubt been derived from coal, petroleum, and decomposing organic matter. It consists of marsh-gas and other hydrocarbons.

PETROLEUM.

Occurrence.—Petroleum occurs in many parts of the earth. It is particularly abundant in the Appalachian and interior coal-fields of North America and in Russia on the shores of the Black and Caspian seas. These two regions produce about nine tenths of the world's supply. It is also found in California, Texas, and other States, and in Persia, Burmah, China, Japan, Hungary, Germany, and parts of South America.

Properties.—Petroleum is a thick, oily, fluorescent liquid with an unpleasant odor and specific gravity 0.78 to 0.90. It is yellow or greenish in color and sometimes nearly black.

Origin.—The origin of petroleum is not known. It was most probably produced by the decomposition of organic matter away from the air. It is usually, though not always, associated with coal. The California petroleums are supposed to be of animal origin. Another theory is that it has been the result of the decomposition of metallic carbids by heat in the presence of water.

Composition.—American petroleum consists almost entirely of hydrocarbons of the marsh-gas series, while the Russian oil contains 10 per cent of benzene compounds, with a notable quantity of ethylene. The liquids hold the gases and solids in solution.

Refining.—Petroleum is refined by fractional distillation. In the first process it is separated into four parts.

1. *Petroleum ether*, boiling below 60° and consisting mostly of pentane and hexane. This is further divided into two or three products, the chief of which is *gasoline*, which boils at 46° and has a specific gravity about 0.65.

2. *Petroleum benzene* or *naphtha*, boiling between 60° and 120°, and consisting mainly of heptane and octane. It is separated into benzine which boils about 60° and has a specific gravity about 0.7, and two or three grades of naphtha.

3. *Burning oils*, boiling from 150° to 300° and having a specific gravity 0.7 to 0.82. These are usually separated into three grades:

Standard white, with fire test 44° and boiling-point about 175°.
Prime white, with fire test 49° and boiling-point about 200°.
Water white, with fire test 66° and boiling-point about 275°.

The fire test is the temperature at which the oil gives off an inflammable vapor. The oil is gradually heated in a tube or open

vessel until on the approach of a flame the vapor burns with a flash when the temperature is noted.

A good burning oil should be free from the lighter hydrocarbons so that no inflammable gas may arise from its surface, and from the heavier liquids and solids so that the wick may not be clogged.

4. *A residuum* from which is obtained successively lubricating oils, vaselin, paraffin, and finally an excellent coke used for electric purposes.

Asphalt is probably an oxidized residuum of petroleum.

COMPOUNDS OF CARBON WITH THE HALOGENS.

The halogens enter along with hydrogen into the composition of many carbon compounds and all the hydrogen may be replaced by the halogen. We can treat in this connection only the tri and tetra-halids.

Carbon Tetrafluorid, CF_4, is a colorless condensible gas, and the only carbon halid which can be prepared by direct union of the elements. It is formed by the action of fluorin upon finely divided carbon, as lampblack, and the action is attended with light and heat.

Carbon Tetrachlorid, CCl_4, is formed by the action of chlorin upon chloroform in sunlight, $CHCl_3 + Cl = CCl_4 + H$; or by the action of chlorin upon carbon disulfid at 40°. It is a colorless volatile liquid of pleasant odor and specific gravity 1.63. It boils at 76° and becomes a crystalline solid at −30°.

Trichlormethane, or **Chloroform,** $CHCl_3$, is a colorless volatile liquid used as an anesthetic.

Carbon Tetrabromid, CBr_4, is a crystalline solid which melts at 92.5° and boils with decomposition at 189°. It is formed by the action of iodin bromid upon bromoform, $CHBr_3$, or carbon disulfid.

Tribrommethane, or **Bromoform,** $CHBr_3$, is a colorless volatile liquid.

Carbon Tetraiodid, CI_4, crystallizes from ethereal solution in regular octahedrons which have a reddish color. It has specific gravity 4.32, and decomposes on exposure to the air, or on being heated, into carbon dioxid and iodin.

Triiodomethane, CHI_3, or **Iodoform,** is a yellow crystalline solid.

OXIDS OF CARBON.

Carbon forms two oxids:

Carbon monoxid or carbonous oxid,   CO   C=O or O=C=

Carbon dioxid or carbonic oxid, CO_2 O=C=O.

In the first carbon seems to be a dyad, but CO may be regarded as a bivalent radical, and in most cases it seems to act in this way.

CARBON MONOXID.

Formula CO.   Molecular weight 28.   Density 14.

Occurrence.—Carbon monoxid occurs in nature only as it is formed by the imperfect combustion of carbon. It is found in chimney and furnace gases and in the gases coming from charcoal fires.

Preparation.—Carbon monoxid is obtained, always through the aid of heat—

1. By reducing carbon dioxid with carbon, zinc, iron, etc.:

$$CO_2 + C = 2CO.$$
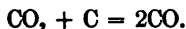
Carbon dioxid is passed through a tube containing charcoal or the metal raised to a red heat. The blue flame which plays over a bed of glowing coals is due to the burning of CO to CO_2. The air entering below forms CO_2. This passing through the hot coals is reduced to CO, which on meeting the air above burns again to CO_2.

2. By the action of water or metallic oxids upon carbon:

$$H_2O + C = H_2 + CO.   \text{(Water-gas.)}$$
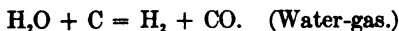
3. By the action of carbon or metals upon carbonates:

$$4CaCO_3 + 3Fe = Fe_3O_4 + 4CaO + 4CO.$$

4. By the action of strong sulfuric acid upon potassium ferrocyanid:

$$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = FeSO_4 + 2K_2SO_4 + 3(NH_4)_2SO_4 + 6CO.$$

5. By dehydrating certain organic acids with hot sulfuric acid:

$$\text{Formic acid, } HCOOH = H_2O + CO.$$

6. In the distillation of organic substances. $HCN + H_2O = CO + NH_3$
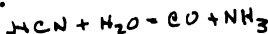
To prepare carbon monoxid for use in the laboratory, heat in a flask one part oxalic acid and six parts sulfuric acid, or one part potassium ferrocyanid and ten parts sulfuric acid. Collect over water or by displacement. If it is desired to have it free from carbon dioxid, let the gas be passed through potassium hydroxid solution.

Physical Properties.—Carbon monoxid is a colorless, tasteless gas with a faintly pungent odor and specific gravity 0.97. It is

slightly soluble, 100 volumes of water dissolving only 3 volumes at 0°. It is one of the most difficult of gases to liquefy. Its critical temperature and pressure are $-140°$ and 36 atmospheres. The liquid boils at $-190°$ and becomes solid at about $-200°$. By allowing it to vaporize *in vacuo* a temperature of $-220°$ is obtained.

Chemical Properties.—Carbon monoxid is not easily formed by direct union of its elements, nor is it easily decomposed. Burning bodies are extinguished in it, and it is chemically quite inactive at the ordinary temperature. It burns with a pale-blue flame to CO_2 and is a powerful reducing agent. Perfectly dry carbon monoxid and oxygen do not unite. The contact or catalytic action of water seems to be necessary, the CO being oxidized by the oxygen of the water and the liberated hydrogen uniting with the free oxygen. Its heat of formation is 29,000 calories.

Physiological Properties.—Carbon monoxid is a violent poison, one per cent in the air producing headache and vertigo, and a larger quantity causing death in a short time. In the blood it unites with the red corpuscles forming *carbonyl hæmoglobin*. This prevents the absorption of oxygen and brings on suffocation. It is found in coal-mines after explosions of methane, and in illy ventilated rooms in which stoves are used and allowed to get red-hot.

Carbonyl Compounds.—Carbon monoxid forms no acid, but as a radical enters into many compounds mostly organic. At 100° it is absorbed by potassium hydroxid to form potassium formate, $\dfrac{K-O}{H}>CO$, from which is obtained formic acid, $\dfrac{H-O}{H}>CO$, an example of organic acids which contain the univalent radical (COOH)' called *carboxyl*.

Carbonyl Chlorid, $COCl_2$, called *phosgene-gas*, is formed by the action of sunlight upon a mixture of carbon monoxid and chlorin. It is a colorless, suffocating gas which is decomposed by water:

$$COCl_2 + H_2O = CO_2 + 2HCl.$$
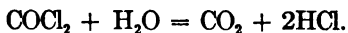
Carbonyl Diamid, Carbamid, or Urea, $CO(NH_2)_2$, is the most important solid excreted by the kidneys.

Metallic Carbonyls.—Carbon monoxid forms with certain metals peculiar compounds called *carbonyls*. With finely divided nickel it gives $Ni(CO)_4$, a colorless, mobile liquid which boils at 43° and has specific gravity 1.36. *Iron carbonyl,* $Fe(CO)_4$, is a pale yellow liquid of specific gravity 1.47 which boils at 102.8°.

Illustrations.—To show how carbon monoxid burns, ignite a jar of the gas or a jet coming from the generator.

To show its action with chlorin, fill two cylinders with the gases, place them mouth to mouth and mix. Expose to sunlight; the color of the chlorin soon disappears, and on separating the cylinders dense fumes appear of HCl formed by the action of moisture upon the carbonyl chlorid.

CARBON DIOXID.

Formula CO_2. Molecular weight 44. Density 22. Liter weighs 1.97 grams.

Occurrence.—Carbon dioxid is a varying constituent of the atmosphere, being continuously produced by combustion, respiration and decay, and continuously removed by the rains, by the alkalies in the atmosphere, and by plant growth. The amount varies from 0.03 per cent to 0.06 per cent by volume and averages about 0.04 per cent, or 4 parts in 10,000 of air. It comes from the earth through fissures and collects in caves, mines, and wells, and is called *choke damp*. The Poison Valley in Java is an old volcanic crater which keeps filled with the gas. The Grotto del Cane, near Naples, fills from fissures in the floor to a depth of 2 to 3 feet, so that a man standing erect breathes the purer air above while a dog is suffocated in the gas below. Liquid carbon dioxid is found inclosed in cavities in crystals of certain rocks, especially quartz.

Carbon dioxid is found in solution in all terrestrial waters, and some springs and wells are so heavily charged with it that they are effervescent and have an acid taste. These are called *carbonated waters* and good examples are seen in Saratoga Springs, N. Y. It is carbon dioxid which holds in solution certain minerals such as limestone and iron.

Combined, carbon dioxid forms the native carbonates of which examples are limestone, $CaCO_3$, dolomite, $CaMg(CO_3)_2$, magnesite, $MgCO_3$, witherite, $BaCO_3$, and siderite, $FeCO_3$.

History.—Van Helmont, early in the seventeenth century, observed that the gas coming from burning wood and fermenting liquids would extinguish fire, and called it *gas sylvestre, wood-gas*. In 1755. Black obtained it from alkali carbonates and called it *fixed air*. Lavoisier proved that it contained carbon and oxygen, and Dalton showed that it contained two atoms of the latter to one of the former. It was liquefied by Faraday and solidified by Thilorier.

Preparation.—Carbon dioxid is formed—

1. By complete combustion of carbon, either free or in its compounds:
$$C + O_2 = CO_2. \quad CH_4 + 2O_2 = 2H_2O + CO_2.$$
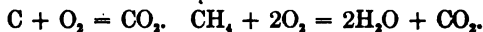
2. By the action of acids upon carbonates:
$$2HCl + CaCO_3 = CaCl_2 + H_2O + CO_2.$$

3. By respiration, fermentation of sugar, and decay of organic substances: Sugar, $C_{12}H_{22}O_{11} + H_2O = 4CO_2 + 4C_2H_6O$, alcohol.

Carbon dioxid is most conveniently prepared from a carbonate, such as marble or soda, by the action of dilute hydrochloric acid. Bits of marble, chalk, or soda are placed in a flask and the acid added through a funnel tube as required. The gas is collected by displacement or over water.

Physical Properties.—Carbon dioxid is a colorless gas with a weak acid taste and a faintly pungent odor. It is heavier than air, having a specific gravity 1.527 and density 22. It may be collected by displacement and poured from one vessel to another. Water dissolves its own volume of carbon dioxid at 14° and 1.79 volumes at 0°. Under increased pressure the volume dissolved is the same, but since gases are reduced in volume by pressure, the quantity dissolved increases in proportion to the pressure. When the pressure is removed, the excess of the gas escapes with effervescence. This action is familiar in soda-waters, carbonated waters, and champagne, all of which have been saturated with carbon dioxid under high pressure. A freshly prepared solution gives off the gas more readily than one which has stood for a long time. In the latter case the carbon dioxid and water seem to have united more firmly as carbonic acid, H_2CO_3.

Carbon dioxid is rather easily liquefied. Its critical temperature and pressure are 31° and 75 atmospheres. At 0° it condenses under 38.5 atmospheres. It forms a colorless, mobile liquid, whose specific gravity changes rapidly with change of temperature, being 0.923 at 0°, 0.868 at 10°, and 0.782 at 20°. If the liquid inclosed in a sealed tube be heated to the critical temperature, 31°, it passes to the gaseous state, the surface line of the liquid gradually fading away. On cooling, the liquid reappears. The liquefied gas put up in strong iron cylinders is an article of commerce.

If liquid carbon dioxid be allowed to escape through a jet into a vessel, the temperature is so lowered by its sudden expansion and partial evaporation that it becomes a snow-like solid which melts

under pressure at $-65°$ and boils under atmospheric pressure at $-78.2°$. The solid is a poor conductor of heat and passes slowly to vapor without melting, because the tension of its vapor at the melting-point, $-65°$, is 3.5 atmospheres. Mixed with ether and evaporated in vacuo, it lowers the temperature to $-140°$. The solid may be handled without hurt, because it is surrounded by a layer of the vapor which prevents actual contact with the hand, but if it be pressed close to the skin it produces painful burns.

Chemical Properties.—Carbon dioxid does not burn, since it is already completely oxidized; and it does not support combustion because of the vigor with which it holds its oxygen. Air containing 1 per cent of it is unfit for respiration, and air containing 2.5 per cent, if the oxygen is correspondingly reduced, will extinguish flame. It is partially decomposed by the electric spark. In contact with combustibles at a high temperature it loses half its oxygen; and at red heat it reacts with certain metals, as potassium and magnesium, yielding the carbonate and free carbon, $K_4 + 3CO_2 = 2K_2CO_3 + C$. It unites directly to water to form carbonic acid and to oxids and hydroxids to form carbonates. Its aqueous solution is a rather powerful solvent for certain minerals, particularly the carbonates of calcium, magnesium, and iron. This is illustrated in chalybeate and limestone waters, from which the carbonates are precipitated by boiling off the free carbon dioxid.

Illustration.—The composition of carbon dioxid may be shown by burning carbon in a vessel of oxygen over mercury, the carbon being held in a platinum boat and ignited by an electric current. The volume of gas after combustion is the same as before, showing that a molecule of carbon dioxid contains a molecule, or two atoms, of oxygen. .

Physiological Properties.—Carbon dioxid is not poisonous. An animal breathing it is suffocated simply from want of oxygen. It is expired from the lungs, and air once breathed is not fit to be breathed again, not so much because of the CO_2 which it contains as because of the diminished quantity of oxygen and the presence of certain other gases and vapors. Taken into the stomach it is tonic and laxative. .

Tests.—The common tests for carbon dioxid are its incombustibility and the precipitate which it produces with lime water.

Uses.—Carbon dioxid is the principal food of plants, being the source of their carbon. It is absorbed by the leaves and built up

with water, through the agency of protoplasm and sunlight, into starch, which is transformed first into sugar and then into cellulose, the main constituent of the plant body. The solvent action of water upon rocks and soils is greatly increased by the presence of CO_2. In the atmosphere it prevents radiation of heat from the earth's surface and acts as a blanket to make the nights and winters less cold than they otherwise would be. It is used in the laboratory in many operations where an inert gas is desired, and in the liquid and solid state for the production of cold.

Illustrations.—The properties of carbon dioxid may be shown by numerous experiments:

1. Heaviness.—Pour from one vessel to another. Drop a soap-bubble into a jar of the well-washed gas; it floats. Balance a beaker on a scale-pan and fill it with CO_2. Draw from a tubulated bottle, like water from a faucet.

2. Effect upon combustion.—Lower into a jar of the gas a lighted taper. Extinguish a candle-flame by pouring the gas upon it. Lower into a jar of the gas a piece of burning magnesium ribbon. Fill a cylinder over water with air from the lungs and test with flame. Pass CO_2 through a heated tube containing a bit of potassium. The potassium burns and carbon is deposited.

3. To show its presence.—Pass through lime-water (a) common air, (b) air from the lungs. Hold a cylinder over a flame for a minute and add lime-water. The lime is first precipitated, but if the passage of the gas be continued is redissolved.

4. Solid and liquid carbon dioxid.—If apparatus for condensing the gas is not at hand, a bottle of the liquid may be purchased. The solid is obtained by allowing the liquid to flow out into a cloth bag, from which it is transferred to a wooden or paper box.

To show the freezing of water, place a tin vessel upon a moistened surface and drop into it a small quantity of the solid CO_2. The vessel will at once be frozen to the surface. To show the freezing of mercury, place a few globules in a dish lined with paper and add some solid CO_2 and a little water-free ether.

CARBONIC ACID AND CARBONATES.

Carbon dioxid dissolves in water to form weakly acidic, unstable H_2CO_3. The solution has a pleasant, sour taste, is completely decomposed at 100°, and has the general properties of the dioxid.

From carbonic acid are derived normal, acid, pyro, and basic carbonates. When carbon dioxid acts upon soluble hydroxids the carbonate is first formed and then the hydrocarbonate. For

example, with lime water we have a precipitate of calcium carbonate, $CaH_2O_2 + CO_2 = CaCO_3 + H_2O$, which presently disappears because of the formation of the more soluble hydrocarbonate, $CaCO_3 + CO_2 + H_2O = H_2Ca(CO_3)_2$.

The alkali carbonates are soluble in water and are not decomposed by heat, while other carbonates are mostly insoluble and are decomposed at high temperature with liberation of CO_2. Most carbonates effervesce with acids.

Normal Ammonium Carbonate, $(NH_4)_2CO_3$, is obtained by passing ammonia gas through a strong solution of the hydrocarbonate. It is a white crystalline solid which on exposure to the air loses ammonia and passes back to the hydrocarbonate.

Hydrogen Ammonium Carbonate (Ammonium bicarbonate), HNH_4CO_3, in the form of large rhombic crystals is obtained by passing carbon dioxid through a solution of the normal salt. This and the other combine to form the so-called ammonium sesquicarbonate, $(NH_4)_2CO_3,2H(NH_4)CO_3,H_2O$.

Ammonium Carbamate, $\frac{H_4N-O}{H_2N}>CO$, is formed when dry ammonia and dry carbon dioxid are mixed. It is as if a hydroxyl of carbonic acid had been replaced by amidogen, NH_2.

Commercial Ammonium Carbonate is a mixture of hydrogen ammonium carbonate and ammonium carbamate. It is a white fibrous solid which smells strongly of ammonia. The carbamate may be dissolved out with alcohol, or may be converted into the normal carbonate by treating it with ammonia.

COMPOUNDS OF CARBON WITH SULFUR.

Carbon forms but one well-defined compound with sulfur, though others have been described. From this compound, which is CS_2, is formed derivatives similar to those obtained from its analogue, CO_2.

CARBON DISULFID.

Formula CS_2. Molecular weight 76. Density 38.

History.—Carbon disulfid was accidentally discovered by Lampadius in 1796 while heating pyrites with charcoal. Its composition was ascertained by Vauquelin in 1812.

Preparation.—Carbon disulfid is prepared by passing sulfur vapor over red-hot charcoal and condensing the vapor in a cooled receiver, $C + S_2 = CS_2$. Thus prepared it contains sulfur and

hydrogen sulfid. It is now prepared on a large scale in a special electric furnace, devised by Edward R. Taylor of Penn Yan, N. Y., in which the carbon and sulfur are brought together between carbon electrodes.

Physical Properties.—Carbon disulfid is a colorless, volatile, highly refractive liquid of specific gravity 1.292 at 0°. It boils at 46° and solidifies at −116°. When pure it has a peculiar odor which is not pleasant, but the commercial article is quite offensive. It is very slightly soluble in water, but gives to the solution its odor and taste. It mixes with alcohol, ether, and benzene, and is a powerful solvent for many substances which are insoluble in water, such as sulfur, phosphorus, bromin, iodin, rubber, and fats. It is used in extracting essential oils and as a solvent for rubber. The latter solution is employed as a cement for leather.

Chemical Properties.—Carbon disulfid ignites at the very low temperature of 120° and burns with a pale-blue flame to carbon dioxid and sulfurous oxid. Burning in oxygen it emits a brilliant bluish-white light. It dissociates at a bright-red heat. In contact with heated metals it is decomposed, yielding the sulfid of the metal and free carbon: $CS_2 + Zn_2 = 2ZnS + C$. Its heat of formation is −26,000 calories, and its heat of combustion 265,130 calories.

Physiological Properties.—Carbon disulfid is an active poison, the vapor producing death when breathed in considerable quantity, and air containing a small amount works injury to the nervous system when continuously breathed. It is a bactericide and stops fermentation.

Carbon Oxysulfid, COS, is obtained by heating CO_2 with sulfur vapor, or by the action of acids upon thiocyanates:

$$2KCNS + H_2SO_4 + 2H_2O = K_2SO_4 + 2NH_3 + 2COS.$$
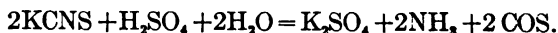
It is a colorless, bad-smelling gas which liquefies at 0° under 12.5 atmospheres. It dissolves in water volume to volume and the solution slowly decomposes, $COS + H_2O = CO_2 + H_2S$. In alkaline solution the decomposition is rapid, $COS + 4KHO = K_2CO_3 + K_2S + 2H_2O$.

THIOCARBONIC ACID AND THIOCARBONATES.

Thiocarbonic Acid, H_2CS_3, is obtained by decomposition of thiocarbonates with hydrochloric acid. It is an unstable yellow liquid with a very offensive odor.

Thiocarbonates are formed by the direct union of metallic sulfids with carbon disulfid: $CS_2 + K_2S = K_2CS_3$; or by the action of carbon disulfid upon hydroxids:

$$3CS_2 + 6KHO = K_2CO_3 + 3H_2O + 2K_2CS_3.$$

Thiocarbonates are all unstable and are decomposed by heat. Those of the alkali and earth metals are soluble in water

Ammonium Thiocarbonate, $(NH_4)_2CS_3$, is a yellow crystalline solid obtained by the action of alcoholic ammonia upon carbon disulfid.

CARBON AND NITROGEN.

Though carbon and nitrogen have but little mutual affinity, they enter together into the composition of many substances, particularly the nitrogenous organic compounds. When these are heated with potassium hydroxid, the compound KCN, called potassium cyanid, is formed. In this compound the postassium unites to the univalent radical, $(CN)'$, in which the nitrogen is triply united, leaving one free point to the carbon atom, $N \equiv C—$. This radical is called *cyanogen*, from a Greek word which means *blue*, referring to the color of one of its important compounds, Prussian blue. It is a negative radical closely related in chemical properties to the halogens and forming similar compounds. It is sometimes represented by the symbol Cy.

CYANOGEN GAS.

Formula C_2N_2. Molecular weight 52. Density 26. Liter weighs 2.33 grams.

History.—Cyanogen was the first compound radical isolated and its discovery made a new era in chemistry. Its compounds had been investigated by Scheele in 1782 and by Berthollet in 1787, but Gay Lussac discovered the radical in 1811 and obtained free cyanogen in 1815.

Preparation.—Cyanogen is liberated in various chemical reactions, but it is most conveniently prepared by heating the cyanid of mercury. silver, or gold, $Hg(CN)_2 = Hg + C_2N_2$; or by strongly heating a mixture of mercuric chlorid and dry potassium ferrocyanid.

It is formed by direct union when the elements are brought together at high temperature, as in the electric arc and blast-furnace.

Physical Properties.—Cyanogen is a colorless gas with a pungent odor resembling that of peach kernels. Water dissolves 4

volumes and alcohol 23 volumes of the gas. At $-20.7°$ it becomes a colorless liquid of specific gravity 0.866, and at a lower temperature it becomes a crystalline solid which melts at $-34.4°$. Its critical temperature and pressure are 124° and 61.7 atmospheres.

Chemical Properties.—The flame of burning cyanogen has a peach-blossom color and the products of the combustion are CO_2 and nitrogen. Chemically it is closely related to the halogens and forms similar compounds. It unites directly to the alkali metals to form cyanids. It and its compounds have a tendency to polymerize, several radicals combining into one molecule.

Cyanogen and all its compounds are violent poisons.

Paracyanogen, $(CN)_x$.—In the preparation of cyanogen from mercuric cyanid, a brown substance is left in the tube. This is found to be a polymer of cyanogen. When strongly heated it dissociates.

Illustrations.—A very simple experiment will illustrate the preparation and properties of cyanogen. Place one gram of mercuric cyanid in a test-tube and heat it. When the gas begins to come off light it at the mouth of the tube. Note the color of the flame. The brown residue in the tube is paracyanogen. Care must be taken not to inhale the gas, as it is a deadly poison.

Tests.—Cyanogen and all its soluble compounds give with a mixture of ferrous and ferric salts a precipitate of Prussian blue.

CYANOGEN COMPOUNDS.

The cyanogen radical is both positive and negative. It forms halids, cyanids, cyanates, and thiocyanates, and is a constituent of many complex compounds both organic and inorganic.

HYDROGEN CYANID, HYDROCYANIC ACID, OR PRUSSIC ACID.

Formula HCN. Molecular weight 27. Density 13.5.

History and Occurrence.—Hydrocyanic acid was discovered by Scheele in 1782. It occurs free in all parts of the Java tree, and its salts are found in many plants, such as the cherry, peach, laurel, and almond.

Preparation.—Hydrogen cyanid is formed by the action of acids upon cyanids: $2KCN + H_2SO_4 = 2HCN + K_2SO_4$.

In the laboratory it is conveniently obtained by heating together in a flask a mixture of 14 parts of water and 7 parts of

sulfuric acid with 10 parts of potassium ferrocyanid. The gas is condensed in a cold tube or conducted into water to form the solution. The reaction is

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe_2(CN)_6 + 6HCN.$$

Physical Properties.—Hydrogen cyanid is a colorless volatile liquid with specific gravity 0.7.   It has the odor of bitter almonds, boils at 26.5°, and forms a crystalline solid which melts at − 15°.   It mixes in all proportions with water, alcohol, and ether. The aqueous solution is the *hydrocyanic* or *prussic acid* of commerce.   It slowly decomposes.

Chemical Properties.—Hydrocyanic acid is weak' and slightly dissociated. The colorless cyanid ion CN′ is very active and forms compounds similar to those of the halogens. It precipitates silver from its solutions as silver cyanid. Its heat of formation is − 34,000 cal.

Hydrocyanic acid is one of the most violent of poisons.   A single drop upon the tongue will cause death in a few seconds.   Smaller quantities produce headache, vertigo, and dyspnœa. It is a constituent of several medicinal preparations, such as laurel water and bitter-almond water.

Cyanids.—The cyanids are unstable, being readily decomposed even by weak acids, such as carbonic acid. They therefore smell of hydrogen cyanid and many of them have an alkaline reaction. The cyanids of the alkalis and alkali-earth metals are soluble in water and are as poisonous as hydrocyanic acid; the others, except $Hg(CN)_2$, are insoluble in water, but dissolve in the alkali cyanids to form double salts; as AgCN,KCN.

Ammonium cyanid, NH_4CN, is formed by the direct union of hydrogen cyanid and ammonia. It crystallizes in colorless cubes, sublimes with partial dissociation at 40°, and is a violent poison.

CYANIC AND THIOCYANIC ACIDS.

Cyanogen as a negative radical forms acids with oxygen and sulfur.

Cyanic Acid, HCNO, or $H—O—C \equiv N$, is a colorless liquid obtained by heating its polymer, **Cyanuric Acid,** $H_3C_3N_3O_3$, and condensing the vapor with the help of a freezing mixture. Its salts, the *cyanates*, are formed when cyanogen gas is conducted into an alkali solution:

$$C_2N_2 + 2KHO = H_2O + KCN + KCNO.$$
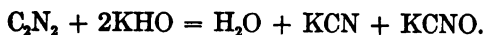
Thiocyanic Acid, HCNS, or H—S—C≡N, is a colorless liquid obtained by action of dry hydrogen sulfid upon mercuric thiocyanate:

$$Hg(CNS)_2 + H_2S = HgS + 2HCNS.$$
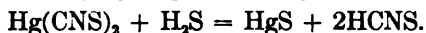
The *thiocyanates* are formed by the direct action of sulfur upon the cyanids. Thus potassium thiocyanate is obtained by heating together potassium cyanid and sulfur: $KCN + S = KCNS$.

CYANOGEN HALIDS.

Cyanogen acts as a positive radical in uniting to various negative elements and radicals. The simple halids are as follows:

Cyanogen chlorid, CNCl, a colorless liquid.

Cyanogen bromid, CNBr, a colorless liquid.

Cyanogen iodid, CNI, a crystalline solid.

These three compounds are very poisonous, have a pungent odor, and emit a vapor which painfully affects the eyes.

SILICON.

Symbol Si. Atomic weight 28. Valence IV. Specific gravity 2.15 to 2.49. Melting-point 1500°.

Occurrence.—Silicon does not occur free. Combined it is the most abundant element after oxygen. Its most important compound is the oxid, SiO_2, which assumes a variety of forms: as quartz, flint, sand, jasper, agate, chalcedony, and chert. Silicates are complex compounds of silicic oxid with various bases: as sodium, potassium, magnesium, calcium, iron, aluminum, etc. Examples are feldspar, hornblend, pyroxene, mica, talc, and clay. At least one fourth part of the surface rocks is silicon.

History.—Silicon was first isolated by Berzelius in 1810 by fusing together iron, carbon, and quartz. The name is from the Latin *si-ex, flint.*

Preparation.—Amorphous silicon may be prepared—

1. By heating potassium fluosilicate with potassium or sodium:

$$K_2SiF_6 + 4K = 6KF + Si.$$
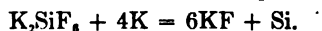
The potassium fluorid is dissolved away with water.

2. By passing silicon fluorid over red-hot sodium:

$$SiF_4 + 4Na = 4NaF + Si.$$
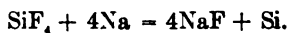
3. By heating an intimate mixture of magnesium and quartz:

$$2Mg + SiO_2 = 2MgO + Si.$$
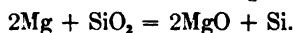
The magnesium oxid is dissolved away with dilute acid.

Crystallized silicon is obtained—

1. By passing vapor of silicon chlorid over aluminum melted in an atmosphere of hydrogen: $3SiCl_4 + 4Al = 2Al_2Cl_6 + 3Si$. The aluminum chlorid is carried away as vapor and the silicon remains as needle-shaped crystals.

2. By dissolving amorphous silicon in melted zinc, and after cooling, dissolving the zinc away with hydrochloric acid.

Physical Properties.—Silicon presents two allotropic forms, one amorphous and the other crystalline.

Amorphous silicon is a brown powder of specific gravity 2.15. It is insoluble in water and all the acids except hydrofluoric. When heated in the air it becomes denser and graphitic in appearance, and this has been described as a third allotropic form.

Crystalline silicon forms steel-gray modified rhombic octahedrons of specific gravity 2.34 to 2.49, and hard enough to scratch glass. It is insoluble in water and acids except a mixture of nitric and hydrofluoric acids.

Chemical Properties.—Silicon burns in air or oxygen to SiO_2, but not completely, since the coating of oxid formed stops the combustion. It burns also in fluorin and chlorin. It dissolves in hydrofluoric acid to form fluosilicic acid, H_2SiF_6, and in sodium or potassium hydroxid to form the silicate K_2SiO_3 or Na_2SiO_3, with liberation of hydrogen in both cases.

COMPOUNDS OF SILICON.

Silicon is wholly acidic, and its only valence is four. It is quite active and forms numerous compounds, most of which are very stable. It does not unite atom to atom like carbon, but links with alternate atoms of oxygen to form molecules of great complexity.

HYDROGEN SILICID.

Formula H_4Si. Molecular weight 32. Density 16. Liter weighs 1.43 grams.

History and Preparation.—Hydrogen silicid was discovered by Buff and Woehler in 1857. It is most conveniently prepared by the action of hydrochloric acid upon magnesium silicid:

$$Mg_2Si + 4HCl = 2MgCl_2 + H_4Si.$$
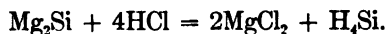
The magnesium silicid is placed in a bottle completely filled with water and provided with a funnel tube which reaches to the bottom, and a wide delivery-tube which dips in a vessel of water. The acid is poured through the funnel tube. As the bubbles of gas escape they take fire with slight explosion, making rings of silicic oxid.

Properties.—Hydrogen silicid is a colorless gas which takes fire spontaneously when gently warmed, or when mixed with hydrogen, or in contact with chlorin.

The compound Si_2H_6 has been prepared by Moissan. It is a liquid which boils at 52° and is solid at −138°.

Silicids.—Many of the metals unite to silicon when heated with it in the electric furnace. Some of the silicids are CSi, Fe_3Si, Mn_2Si, Ni_2Si, Cu_2Si, Pt_2Si, etc.

HALIDS OF SILICON.

Silicon forms two series of compounds with the halogens:

| Tetrahalids, | SiF_4 | $SiCl_4$ | $SiBr_4$ | SiI_4. |
| Hexahalids, | Si_2F_6 | Si_2Cl_6 | Si_2Br_6 | Si_2I_6. |
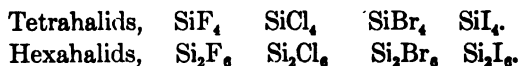
Silicon fluorid, SiF_4, is obtained—

1. By direct union of the elements.
2. By the action of sulfuric acid upon a mixture of calcium fluorid and silicic oxid: $2H_2SO_4 + 2CaF_2 + SiO_2 = 2CaSO_4 + 2H_2O + SiF_4$. An excess of sulfuric acid must be present to absorb the water produced. The gas may be collected over mercury.

The mixture is placed in a test-tube or small flask furnished with a wide delivery-tube, which dips under mercury covered with water. The mercury is to prevent the stopping of the tube with silicic acid. As the bubbles of gas come in contact with the water, decomposition takes place, resulting in the formation of silicic and fluosilicic acids, the first of which appears as a gelatinous precipitate, while the second goes into solution. The reaction is:

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4.$$
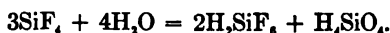
Silicon fluorid is a colorless gas with a pungent odor. It liquefies at −100° and solidifies at −140°.

Fluosilicic acid, H_2SiF_6, or $\begin{matrix} H-F=F \\ \\ H-F=F \end{matrix} \!\!\!>Si<\!\!\! \begin{matrix} F \\ || \\ F \end{matrix}$, is formed by the

action of water upon silicon fluorid, as indicated above. It is known only in solution, as it dissociates when evaporated. It is dibasic, dissolves metals, and forms salts. The 10 per cent solution has specific gravity 1.08; 5 per cent 1.04.

Fluosilicates.—The fluosilicates are generally soluble in water. Those difficultly soluble are the fluosilicates of sodium, potassium, lithium, barium, calcium, and yttrium. The strontium salt is soluble, and so the acid is used to separate barium from strontium.

Silicon Hexafluorid (Trifluorid), Si_2F_6, is a white powder obtained by passing silicon fluorid over heated silicon.

Silicon Chlorid, $SiCl_4$, is obtained by direct union of the elements, or by heating a mixture of carbon and silicic oxid in a stream of chlorin:

$$SiO_2 + 2C + 2Cl_2 = 2CO + SiCl_4.$$

It is a colorless fuming liquid of specific gravity 1.52 and boiling-point 58.2°. It is decomposed by water into hydrochloric and silicic acids.

Silicon Hexachlorid (Trichlorid), Si_2Cl_6, is obtained by passing $SiCl_4$ over strongly heated silicon, or by gently heating silicon hexaiodid with mercuric chlorid. It is a colorless, fuming, inflammable liquid of specific gravity 1.58, melting-point − 1°, and boiling-point 146°.

Trichlor-hydrogen Silicid (Silicon chloroform), $SiHCl_3$, is a colorless, fuming, inflammable liquid which boils at 36°. It is obtained by heating silicon in a current of dry hydrogen chlorid.

Silicon Oxychlorid, Si_2OCl_6, is a colorless fuming liquid formed by the action of silicon chlorid upon felspar. It boils at 137° and is decomposed by water.

Silicon Bromid, $SiBr_4$, is obtained by leading bromin over a heated mixture of carbon and silicic oxid. It is a colorless liquid of specific gravity 2.8. It boils at 154° and solidifies at 13°. It is decomposed by water into hydrobromic and silicic acids.

Silicon Hexabromid, Si_2Br_6, is obtained by treating silicon hexaiodid with bromin in the presence of carbon disulfid. It is a crystalline solid which distils at 240°.

Silicon Brom-trichlorid, $SiBrCl_3$, is formed by the action of bromin upon silicon chlorid at 100°. It is a colorless liquid which boils at 80°.

Silicon Iodid, SiI_4, is formed by direct union of the elements, or by leading a stream of iodin vapor and carbon dioxid over heated silicon. It forms colorless crystals which melt at 120.5° and boil at 290°. It burns in the air and is decomposed by water into hydriodic and silicic acids.

Silicon Hexaiodid, Si_2I_6, is formed by heating to 280° a mixture of silicon iodid and finely divided silicon. It is a fuming, crystalline solid which is decomposed by water.

Tri-iodo Hydrogen Silicid (Silicon iodoform), $SiHI_3$, is obtained by passing hydrogen and hydrogen iodid over heated silicon. It is a colorless mobile liquid which boils at 220° and has a specific gravity 3.36.

SILICIC OXID (SILICA).

Formula SiO_2. Molecular weight 60. Specific gravity 2.2 to 2.6.

Silicon forms but the one oxid, SiO_2, commonly called *silica.*

This and its compounds, the silicates, make up the greater portion of terrestrial rocks.

Preparation.—Amorphous silicic oxid is obtained by burning silicon, or by igniting silicic acid:

$$Si + O_2 = SiO_2. \quad H_2SiO_3 = H_2O + SiO_2.$$

Crystallized silicic oxid is obtained by cooling a hot solution of an acid silicate. When an alkaline silicate solution is heated in a closed glass tube, the glass is dissolved and on cooling, the silicic oxid is deposited in minute crystals, quartz when the temperature is above 180° and tridymite when it is below this. In some such way it is probable that native quartz has been formed.

Physical Properties.—Silicic oxid presents three forms: crystalline, cryptocrystalline or compact, and amorphous.

1. *Crystalline varieties.*—Crystalline silicic oxid is dimorphous in two closely related forms, *quartz* and *tridymite*.

a. Quartz commonly occurs in hexagonal prisms, surmounted by hexagonal pyramids. The prisms are of two kinds, scarcely distinguishable by the eye. differing in that the one turns the plane of polarization to the right and the other to the left when polarized light is passed parallel to the vertical axis. The first is called right-handed or positive, and the second left-handed or negative crystals. Pure quartz is colorless and transparent, and when cut and polished is second in brilliancy only to the diamond. It is therefore used as a gem under various names, as *California diamonds, Colorado diamonds*, and *Rhinestones*. It is also used for fine lenses for optical instruments and spectacles, and is called *pebble glass*. It is harder than glass and is infusible before the blowpipe, but melts in the oxy-hydrogen flame and may be drawn out into very fine threads. It is insoluble in water and is one of the most stable and unchangeable of all native substances. It has specific gravity about 2.6 and presents several varieties, due to the presence of impurities and coloring matters.

Quartz crystal, colorless and transparent.
Smoky quartz, smoky, with dark and gray colors.
Rose quartz, compact .and rosy in color.
Amethyst, colored a beautiful purple.
Milky quartz, milky in appearance and more or less opaque.

b. Tridymite is found in various rocks, particularly in trachytes.

It forms hexagonal tablets and one-sided twin crystals.   It has the hardness of quartz, but specific gravity only 2.3.

2. *Cryptocrystalline varieties.*—These have a waxy luster, a concoidal fracture, the hardness of quartz, and a specific gravity 2.3. They are generally hydrous, containing varying quantities of water. They are opaque and vary in color from white through greens and reds to black.   The principal varieties are:

Chalcedony, white, gray, brown to black.
Carnelian, red or brown.
Prase and chrysoprase, green.
Agate, a variegated chalcedony.
Moss agate, filled with mossy, dendritic forms.
Onyx, agate, with layers of different colors.
Sardonyx, like onyx, but with layers of carnelian.
Jasper, impure, opaque, and variously colored.
Flint, compact and in dull colors.
Hornstone, more brittle and not so compact as flint; called also chert.

Lydian stone, or touchstone, a black, velvety jasper used for trying precious metals, the color of the mark on the stone indicating the amount of alloy.

3. *Amorphous silica.*—Artificially prepared, this is a soft white powder of specific gravity 2.2.   To this variety may also be referred the silicious sinter deposited from solution in water and silica which is of vegetable and animal origin, examples of which are the flint nodules in chalk which are composed of shells and spicules of Radiolarians, and *diatomaceous* or *infusorial earth*, which is found in large deposits in various countries, especially in Germany, where it is called *kieselguhr*.   The last is used as a polishing powder and the absorbent with which nitroglycerin is mixed to make dynamite.

Opal is a compact amorphous silicic oxid, a little softer than quartz and more easily attacked by hydrofluoric acid, and usually hydrous.   It is of all colors, red, yellow, blue, green, and brown predominating.   It exhibits a rich peculiar iridescent play of colors known as *opalescence*.   Some of the principal forms are:

Precious opal, pure in color and opalescence and a beautiful gem.
Fire opal, hyacinthan red or honey yellow with fiery reflections.
Common opal, translucent, white, blue, yellow, green, or red.
Wood opal, wood petrified as opal.
Floatstone, so light and spongy as to float on water.

Chemical Properties.—Silicic oxid is very stable, and is not affected by air or water. It dissolves in alkalis to form alkaline silicates, and in this form is found in many hot waters. On exposure to air these waters deposit it as a white amorphous sinter. Such deposits are abundant in the vicinity of hot springs and geysers. When fused with alkaline carbonates, it forms soluble silicates called water-glass: $SiO_2 + 2Na_2CO_3 = 2CO_2 + Na_4SiO_4$. Its heat of formation is 219,240 calories.

SILICIC ACIDS.

Silicic oxid is insoluble in water, but by indirect methods a series of acids is formed which as a rule cannot be isolated, but are well represented in their salts, the silicates.

Orthosilicic Acid, H_4SiO_4.—When hydrochloric acid is added to a dilute solution of an alkaline silicate, silicic acid is formed, but remains in solution:

$$Na_2SiO_3 + 2HCl + H_2O = 2NaCl + H_4SiO_4.$$
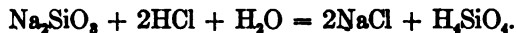
The silicic acid is not in true solution, but is in the colloidal state and may be separated from the sodium chlorid and excess of hydrochloric acid by dialysis. The solution is placed in a dialyzer (made by stretching a piece of parchment or parchment paper over one end of a hoop or short cylinder), and this is floated upon the surface of pure water. The salt and hydrochloric acid diffuse through into the water, while the silicic acid remains in the dialyzer. By renewing the water a few times a pure solution of silicic acid is obtained. This may be concentrated over sulfuric acid until it contains 21 per cent of H_4SiO_4. It is a tasteless liquid with a faintly acid reaction.

Metasilicic Acid, H_2SiO_3.—If the solution of dialyzed silicic acid be further evaporated or allowed to stand for some time, it passes to a jelly-like mass which is not soluble in water. When this is dried it has approximately the composition H_2SiO_3. When it is heated it loses water and becomes amorphous silicic oxid. When hydrochloric acid is added to a strong solution of an alkaline silicate, a gelatinous precipitate falls which is probably metasilicic acid.

Disilicic Acids.—By taking water from two molecules of orthosilicic acid, the series is obtained called *disilicic acids :*

$2H_4SiO_4 - H_2O\ \ = H_6Si_2O_7$, Hexabasic disilicic acid.
$2H_4SiO_4 - 2H_2O = H_4Si_2O_6$, Tetrabasic disilicic acid.
$2H_4SiO_4 - 3H_2O = H_2Si_2O_5$, Dibasic disilicic acid.
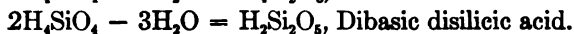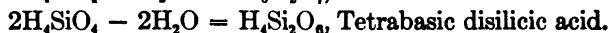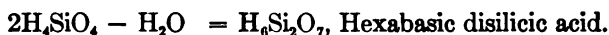
Trisilicic Acids.—In the same manner, by taking water from three molecules we have the *trisilicic acids*, $H_{10}Si_3O_{11}$; $H_8Si_3O_{10}$; $H_6Si_3O_9$; $H_4Si_3O_8$; $H_2Si_3O_7$.

Among the silicates there are derivatives of still more complicated acids, but they may all be regarded as combinations of those already given. The formulas may be variously written and the following are simply suggestions:

Disilicic acids,
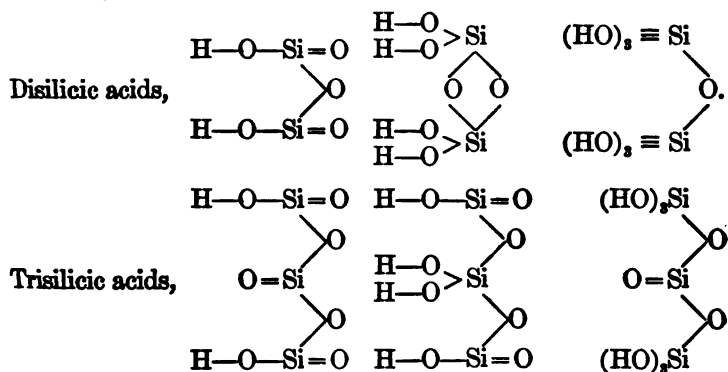
Trisilicic acids,

Silicates.—The numerous and complicated silicates which occur in nature are derivatives of the various silicic acids, the hydrogen being replaced by positive elements. A few examples of the simple compounds may be taken as illustrations:

Orthosilicates: Zircon, $Zr^{IV}SiO_4$; Garnet, $Ca_3''Al_2'''(SiO_4)_3$.
Metasilicates: Wallastonite, $Ca''SiO_3$; Steatite, $H_2Mg_3''(SiO_3)_4$.
Disilicates: Petalite, $NaLiSi_2O_6$; Serpentine, $Mg_3Si_2O_7$.
Trisilicates: Orthoclase (feldspar), $KAl(Si_3O_8)$.

Only the silicates of the alkali metals are soluble in water. The hydrous silicates, called *zeolites*, dissolve in hydrochloric acid with the separation of gelatinous silicic acid. The anhydrous silicates are insoluble in hydrochloric acid. They are rendered soluble by fusing them with alkalis.

SILICON AND SULFUR.

Silicon Sulfid, SiS_2, is obtained by heating amorphous silicon with sulfur, or by passing sulfur vapor over an ignited mixture of carbon and silicic oxid. It forms shiny needles, which are decomposed by water into silicic acid and hydrogen sulfid.

Silicon Chlorhydrosulfid, $SiCl_3SH$, is formed when a mixture of hydrogen sulfid and silicon chlorid is passed through a red-hot tube.

It is a colorless fuming liquid which boils at 96°, and is decomposed by water into hydrogen chlorid, silicic acid, and hydrogen sulfid.

SILICON AND NITROGEN

A compound of silicon and nitrogen is formed by strongly heating silicon in nitrogen, or by the action of ammonia upon silicon chlorid. It is a white amorphous powder which decomposes slowly in the air.

SILICON AND CARBON.

. **Silicon Carbid, or Carborundum,** SiC, is obtained by fusing together silicic oxid and carbon in the electric furnace, $SiO_2 + 3C = 2CO + SiC$. It is a greenish or black solid, which is exceedingly hard and is used as a polishing material. It is very resistant to chemical change, because when placed in the fire the coating of silicic oxid which is formed on the surface protects the material beneath.

GERMANIUM.

Symbol Ge. Atomic weight 72. Molecular weight 144. Valence II and IV. Specific gravity 5.47. Melts at 900°.

Occurrence.—Germanium is a very rare element and does not occur free. Its principal native compound is the rare mineral *argyrodite,* a double sulfid of silver and germanium, $4Ag_2S,GeS_2$.

History.—In 1871, Mendeleeff predicted the existence of an element between tin and mercury and described its properties. He gave it an atomic weight 73, and valence II and IV, and called it *ekasilicon.* In 1886, Winkler, of Freiberg, discovered germanium, whose properties are in striking agreement with those of the hypothetic element of Mendeleeff.

Preparation.—The separation of germanium from its native ore is quite difficult. It is most easily obtained by reducing its oxid with carbon or hydrogen at a red heat.

Physical Properties.—Germanium is a brittle dark-gray powder which melts at about 900° and crystallizes from fusion in brilliant metal-like octahedrons of specific gravity 5.47.

Chemical Properties.—Germanium burns in the air to GeO_2, and in chlorin to $GeCl_4$. It is insoluble in dilute acids, but is oxidized by strong nitric acid to GeO_2, and it dissolves in strong sulfuric acid, probably forming germanous sulfate, a portion of the acid being reduced at the same time to SO_2. It is both negative and positive and has valences II and IV. It forms germanous and germanic binary compounds, but few, if any, ternary salts have been isolated. As a tetrad, it is negative, forming acids and germanates.

GERMANIUM COMPOUNDS.

The compounds of germanium are exactly analogous to those of carbon and silicon. No hydrogen compound of germanium has been prepared and the existence of the fluorid is still doubtful.

Fluogermanic Acid, H_2GeF_6, is a crystalline solid.

Germanic Chlorid, $GeCl_4$, is obtained by burning germanium in chlorin, or by heating germanic sulfid with mercuric chlorid. It is a colorless, fuming, mobile liquid of specific gravity 1.887 at 18°. It boils at 86°, and is decomposed by water into hydrochloric and germanic acids.

Germanium Chloroform, $GeHCl_3$, is produced by the action of hydrogen chlorid upon germanium. It is a mobile liquid which boils at 72°. It decomposes slowly in the air, giving rise to *germanic oxychlorid*, $GeOCl_2$, which is an oily liquid.

Germanium Bromid, $GeBr_4$, is formed when germanium is heated in bromin. It is a fuming liquid which is a crystalline solid at 0°.

Germanium Iodid, GeI_4, is obtained by passing iodin vapor over heated germanium, or by heating germanium chlorid with potassium iodid. It is a yellow deliquescent solid which melts at 144° and boils at 400°.

Germanous Oxid, GeO, is an unstable gray readily oxidizable solid which forms a feebly basic hydroxid, GeH_2O_2.

Germanic Oxid, GeO_2, is formed by the combustion of germanium or germanium sulfid, or by oxidizing germanium with nitric acid, or by decomposing the chlorid with water. It is a stable white powder of specific gravity 4.7. It is slightly soluble in water (1 part to 95), forming an acid solution. It is wholly acidic, not forming salts with the acids.

Germanic Acid, H_4GeO_4, or H_2GeO_3, is formed by the action of water upon the chlorid. It dissolves the alkalis, forming *germanates*.

Germanous Sulfid, GeS, is obtained by careful reduction of the disulfid. It is a dark-gray crystalline solid.

Germanic Sulfid, GeS_2, is formed when hydrogen sulfid is passed through an acid solution of the oxid, or by the action of hydrochloric or sulfuric acid upon its thiosalts. It is a white powder which is insoluble in acids, but makes a colloidal solution in water, from which it is precipitated by acids. It dissolves in alkaline solutions and forms thiosalts with alkaline sulfids, an example of which is *silver thiogermanate*, Ag_2GeS_3.

TIN.

Symbol Sn. Atomic weight 119. Valence II, IV. Specific gravity 7.3. Melting-point 235°.

Occurrence.—Tin has been found free in Siberia, Guiana, Bolivia, and Mexico, but in very small quantities. Its principal native

compound is the mineral *cassiterite* or *tin-stone*, SnO_2. This is found in large deposits in only a few places. The principal localities are Cornwall and Devonshire in England, the island of Banca in the Malay peninsula, Bohemia, Saxony, India, Sweden, South Australia, Bolivia, Peru, and Mexico. Very little is found in the United States. It occurs in veins in granitic rocks. Stream tin consists of water-worn pebbles found in the beds of watercourses. Tin occasionally occurs as a mixed sulfid with other metals. Its associates are arsenic, antimony, iron, copper, zinc, lead, and tungsten. Tin from Banca is chemically almost pure.

History.—Tin has been known from the earliest times. It is a constituent of the implements used by primitive man in the Bronze Age. Pliny called it *plumbum album*, and the name *stannum* dates from the fourth century. It was called *Jupiter* by the alchemists. Herodotus called the British Isles the *cassiterides* or *tin islands*. The word *tin* is Anglo-Saxon.

Preparation.—Tin is prepared by reducing the oxid with carbon:

$$SnO_2 + 2C = 2CO + Sn.$$
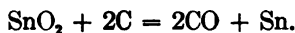
The ore is washed and pulverized and then roasted with free access of air, whereby sulfur and arsenic are driven off, iron oxidized, and copper converted into copper sulfate. The copper sulfate is washed out and the residue heated with carbon in a reverberatory furnace. When the reduction is complete the temperature is brought to the melting-point of tin, and this metal is drawn off, leaving the most of the others behind. It is further purified by remelting and stirring with a stick of green wood, which causes the separation of a scum containing the impurities.

Physical Properties.—Tin is a silver-white solid with metallic luster and specific gravity 7.3. It is softer than zinc and harder than lead, and can be cut with a knife. It is quite malleable, but not very ductile, and has but little tenacity. It may be beaten into sheets one fortieth of a millimeter (one thousandth of an inch) in thickness. This is the *tin-foil* of commerce. It melts at 235° and vaporizes at about 1650°. At 100° it is ductile and at 200° it is brittle and may be pulverized. It is a good conductor of heat and electricity. Its specific heat is 0.0559.

Tin shows a strong tendency to crystallize when cooled from fusion or when separated from its compounds. It is dimorphous, crystallizing in square and rhombic prisms. If a bar of tin be bent,

a peculiar crepitation is heard called the *cry of tin*. This is due to the movement of the crystals one upon the other.

If tin be cooled to a low temperature, $-48°$, it falls to a gray powder of specific gravity only 5.8. This is called *amorphous tin*, and it changes back to the other form on being heated. It is said to undergo the same change slowly at the ordinary temperature. Tin which had been kept three hundred years was found by Schertel so brittle as to be crushed between the fingers.

Illustrations.—Crystals of tin may be obtained in the following ways:
Melt tin and pour off the liquid after the crystals begin to form.
Place a strip of zinc in a solution of tin chlorid. The tin separates in branching crystals called the *tin tree*.
Add slowly to a solution of tin chlorid water containing zinc dust.
Etch a tinned surface with aqua regia.

Chemical Properties.—Tin is unchanged in the air, but tarnishes in the presence of hydrogen sulfid. When strongly heated it burns with a bright light to SnO_2. It dissolves in hydrochloric, sulfuric, and dilute nitric acids to form stannous salts:

$$Sn + 2HCl = H_2 + SnCl_2.$$
$$Sn + 2H_2SO_4 = SO_2 + 2H_2O + SnSO_4.$$
$$4Sn + 9HNO_3 = 3H_2O + NH_3 + 4Sn(NO_3)_2.$$
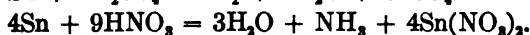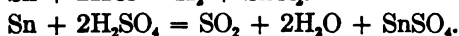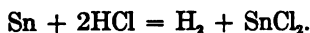
Anhydrous nitric acid does not attack it, but ordinary concentrated acid, specific gravity 1.24, acts upon it with violence, forming metastannic acid:

$$Sn + 4HNO_3 = 4NO_2 + H_2O + H_2SnO_3.$$

Uses.—Tin is very largely used for making alloys, and for covering or *tinning* the surface of other metals, particularly iron, copper, brass, and bronze, to protect them against the action of air and water. Common *tin-plate* is made by dipping sheets of iron in melted tin. The thickness of the coating is increased by *re-dipping*. This is the material of which ordinary tinware is made. *Terneplate* or *lead-tin* is covered with a mixture of lead and tin. It is used for roofing. *Tin-foil* is much used for wrapping various articles of merchandise. The price of tin is about 30 cents a pound.

Alloys of Tin.—Tin forms numerous alloys with other metals, some of which are important articles of commerce.

Tin amalgam is made by pouring mercury into melted tin. It is a liquid, or a granular crystalline solid, according to the proportion

of mercury. It is chiefly employed for silvering the backs of mirrors. Tin-foil is spread upon a level slate table and covered with a thin layer of mercury. The well-cleaned glass plate which is to be silvered is laid upon the surface of the mercury and gradually pressed down to the tin-foil. When the plate is raised the tin-foil adheres and the excess of mercury runs away.

Solder is an alloy of lead and tin: common solder, equal parts; coarse solder, one of tin to two of lead; fine solder, two of tin to one of lead.

Pewter is an alloy of three or four parts of tin to one of lead; sometimes with small quantities of antimony, bismuth, and copper.

Bronzes are made of copper and tin in about the proportion found in gun-metal, but with the addition of two or three per cent of other metals, generally lead and zinc.

Phosphor-bronze.—The addition of phosphorus to bronze makes it hard, tough, and elastic, and the alloy is called *phosphor-bronze.* It is prepared by melting copper with tin phosphid. Sometimes a little lead is added. It contains one to three per cent of phosphorus and five to fifteen of tin.

Speculum metal has one part of tin to two parts of copper. Sometimes a small quantity of arsenic is added. It is brittle, has a steel-gray color, and takes a fine polish.

Bell-metal, used for bells and gongs, has usually four or five parts of copper to one of tin, with addition of small quantities of other metals, as iron, lead, and nickel.

Britannia metal is mainly tin and antimony, with a little copper and zinc. One sample gave tin 86, antimony 10, copper 1, and zinc 3.

Queen's metal has 1 part lead, 1 part bismuth, 1 part antimony, and 9 parts tin.

COMPOUNDS OF TIN.

In appearance and physical properties tin is metallic. In its chemical relations it is both acidic and basic. Its ions are stannous $Sn^{..}$, stannic $Sn^{....}$, stannite SnO_2'', stannate SnO_3'', halostannite, and halostannate. It does not unite to hydrogen. The heat of formation of some of its compounds is as follows:

$$(Sn, Cl_2) = 8080 \text{ cal.}; \quad (Sn, Cl_4) = 12{,}700 \text{ cal.}; \quad (Sn, O) = 6800 \text{ cal.};$$
$$(Sn, O_2) = 13{,}600 \text{ cal.}$$
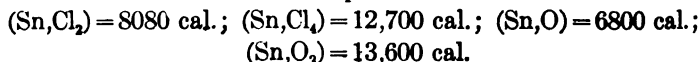
HALIDS OF TIN.

Tin combines with all the halogens, forming usually stannous and stannic compounds, as well as oxy and thio halids. There are also salts of halostannic acid analogous to those of fluosilicic acid; for example, *potassium fluostannate*, K_2SnF_6, or

$$\begin{array}{cc} K—F = F\diagdown & \diagup F \\ & Sn \diagup \diagdown \, || \, . \\ K—F \doteq F\diagup & \diagdown F \end{array}$$

Stannous Fluorid, SnF_2, is obtained by dissolving stannous hydroxid in hydrofluoric acid. On evaporation it separates as small white lustrous monoclinic prisms.

Stannic Fluorid, SnF_4, has not been isolated, but stannic oxyfluorid, $SnOF_2$, has been prepared.

Fluostannic Acid, H_2SnF_6, has not been obtained free, but its salts are well known. Ammonium fluostannate, $(NH_4)_2SnF_6$, crystallizes in rhombohedrons.

Stannous Chlorid, $SnCl_2$, is obtained by dissolving tin in hydrochloric acid. It crystallizes with two molecules of water, forming the tin salt $SnCl_2,2H_2O$, which is used as a mordant in dyeing. The anhydrous salt is prepared by heating tin in dry hydrogen chlorid. It is an amorphous solid which melts at 250° and boils at 606°. The hydrated salt dissolves in a small quantity of water, but on dilution is precipitated as the basic chlorid, $2Sn(HO)Cl,H_2O$.

Chlorostannous Acid, $HSnCl_3$ or H_2SnCl_4, and **Chlorostannites** have been prepared.

Stannic Chlorid, $SnCl_4$, is prepared by passing chlorin over heated tin, or by heating tin with an excess of mercuric chlorid. It is a colorless, fuming liquid of specific gravity 2.27. It was formerly called *spiritus fumans.Libavii*, it having been first prepared by Libavius in 1605. It boils at 114° and solidifies at −33°. It forms various hydrates: $SnCl_4,3H_2O$ is a soft crystalline mass called *butter of tin*, and $SnCl_4,5H_2O$ is the commercial *oxymuriate of tin*.

Chlorostannic Acid, H_2SnCl_6, $6H_2O$, obtained by dissolving $SnCl_4$ in HCl, forms crystals which melt at 28°.

Chlorostannates.—Stannic chlorid combines with metallic chlorids to form chlorostannates similar to the fluostannates. An example is ammonium chlorostannate, $(NH_4)_2SnCl_6$, a crystalline powder formerly used by the calico-printer under the name of *pink salt*.

Stannous Bromid, $SnBr_2$, is formed when tin is heated with hydrogen bromid or mercuric bromid. It is a gray fusible soluble crystalline solid.

Stannic Bromid, $SnBr_4$, is formed by direct union of the elements with the production of light and heat. It is a white crystalline solid of specific gravity 3.32, fumes in the air, dissolves in water, melts at 30° and boils at 201°.

Bromostannic Acid, H_2SnBr_6, and **Bromostannates** have been formed. The latter crystallize with six, eight, or ten molecules of water.

Stannic Bromchlorids of formulas $SnBr_3Cl$ and $SnBrCl_3$ are known.

Stannous Iodid, SnI_2, formed by adding potassium iodid to a warm solution of stannous chlorid, crystallizes in yellow needles.

Iodostannous Acid, H_2SnI_4, and **Iodostannites** have been prepared.

Stannic Iodid, SnI_4, is formed when tin is heated with iodin to 50°. The tin is moistened with carbon disulfid and the iodin added by littles. It crystallizes in red octahedrons, melts at 146°, sublimes at 180°, and boils at 295°.

OXIDS AND HYDRATES OF TIN.

Tin forms two oxids, SnO and SnO_2, both of which act upon acids yielding salts. The hydrates of the first are basic, while those of the second are acidic and give rise to two series of salts called *stannates* and *metatsannates*.

Stannous Oxid, SnO, is obtained by heating stannous hydroxid or stannous oxalate away from the air. It is a brown powder which burns in the air to SnO_2, and is a powerful reducer. It dissolves in the acids yielding stannous salts.

Stannous Hydroxid, SnH_2O_2, is obtained as a white amorphous precipitate when sodium carbonate is added to a solution of stannous chlorid:

$$2SnCl_2 + 2Na_2CO_3 + 2H_2O = 4NaCl + 2CO_2 + 2SnH_2O_2.$$
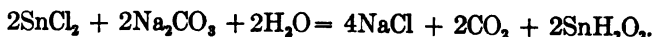
Stannic Oxid, SnO_2, occurs in nature as the mineral *cassiterite*, or *tin stone*, and is the principal ore of tin. It has specific gravity 6.8, and crystallizes in modified square prisms.

Stannic oxid is formed as an amorphous white powder when tin is burned in the air. It is infusible, and insoluble in water, acids, and alkalis.

Orthostannic Acid, H_4SnO_4, is formed when stannic chlorid is treated with a molecular proportion of potassium hydroxid or with an excess of calcium carbonate: $SnCl_4 + 4KHO = 4KCl + H_4SnO_4$. It separates as a white gelatinous precipitate, soluble in acids and alkalis. When dried in vacuo it looses water and becomes H_2SnO_3

(meta), which is the acids from which most stannates are derived. Sodium stannate, $Na_2SnO_3,3H_2O$, is the *preparing salt* of the dyer.

Metastannic Acid, H_2SnO_3.—When tin is dissolved in strong nitric acid, a white amorphous powder separates, which is a polymer of metastannic acid. The formula usually assigned to it is $H_{10}Sn_5O_{15}$. When dried it looses water and finally becomes H_2SnO_3. It is dibasic, and forms salts which are called *metastannates*. Those best known are the sodium and potassium salts.

TIN WITH SULFUR, SELENIUM, AND TELLURIUM.

Stannous Sulfid, SnS, is precipitated from stannous solutions by hydrogen sulfid as a dark-brown amorphous powder. By fusing tin and sulfur together, it is obtained as a gray crystalline mass of specific gravity 4.97. It dissolves in hot hydrochloric acid, giving hydrogen sulfid and stannous chlorid, and in alkaline polysulfids, giving thiostannates.

Stannic Sulfid, SnS_2, is precipitated from stannic solutions by hydrogen sulfid as a yellow amorphous powder. It is obtained in golden-yellow crystalline scales by heating together tin, sulfur, and ammonium chlorid. In this form it is used as a pigment and bronze powder under the name of *mosaic gold*. It dissolves in hydrochloric acid and is oxidized by nitric acid to metastannic acid.

Thiostannic Acid, H_2SnS_3, is obtained by adding hydrochloric acid to solutions of thiostannates. It falls as a yellow precipitate, which on drying gives a dark powder.

Thiostannates are obtained by the action of alkali sulfids and hydrosulfids upon stannic sulfid: $SnS_2 + K_2S = K_2SnS_3$.

Tin forms compounds with selenium and tellurium similar to its compounds with sulfur.

TIN WITH PHOSPHORUS, ARSENIC, AND ANTIMONY.

When tin filings are heated in phosphorus vapor a silver-white mass is obtained which has the composition SnP and a specific gravity 6.56. Phosphorus alloys with molten tin in various proportions. Sn_3P is a coarsely crystalline mass resembling cast zinc. It is used in making phosphor-bronze.

Tin does not form definite compounds with arsenic and antimony; but alloys with them in various proportions.

TIN SALTS.

Tin forms salts with most of the acids, but they are rather unstable and not easily prepared. Very few are of any commercial importance. Those best known are stannous sulfate, $SnSO_4$, stannic sulfate, $Sn(SO_4)_2$, stannous nitrate $Sn(NO_3)_2$, stannic nitrate, $Sn(NO_3)_4$, and stannic phosphate, $Sn_3(PO_4)_4$.

LEAD.

Symbol Pb. Atomic weight 207. Valence II and IV. Specific gravity 11.37. Melting-point 325°. Specific heat 0.0293.

Occurrence.—Lead occurs free very rarely, and in small quantities, having probably been reduced from its compounds by volcanic action. Its principal ore is the sulfid, PbS, known as the mineral *galena*. There are also large deposits of the carbonate, $PbCO_3$, called *cerussite*, and of the sulfate, $PbSO_4$, called *anglesite*. Besides these there are numerous complex compounds of lead with other elements. Its usual associates are silver, gold, copper, and zinc, and the rocks in which it is found are barite, calcite, fluorite, and granite. Its principal American localities are Missouri, Illinois, Wisconsin, Iowa, and the entire Rocky Mountain region.

History.—Lead has been known during all historic time. It has biblical mention in Job and Numbers, and was well known to the Romans. It was called by Pliny *plumbum nigrum*, to distinguish it from silver, which was *plumbum candidum*. It was one of the seven metals of the ancients (gold, silver, copper, tin, lead, iron, mercury), and was assigned to the planet Saturn. Hence lead-poisoning was called *saturnine poisoning*.

Preparation.—The lead of commerce is mostly obtained from galena. There are two general methods of reduction, the first applicable to ores that are comparatively pure, and the second to ores which contain sulfids of iron, copper, zinc, etc.

In the first method the process goes on in two stages. The ore is roasted in a reverberatory furnace, with free access of air, whereby it is partially oxidized to lead oxid and lead sulfate:

$$2PbS + 7O = SO_2 + PbO + PbSO_4.$$
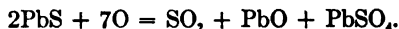
The furnace is now closed, the air excluded, and the temperature raised, whereby the oxid and sulfate are reduced by the lead sulfid which remained unoxidized: $2PbS + PbSO_4 + 2PbO = 3SO_2 + 5Pb.$

In the second method the reduction is affected by heating the lead sulfid with iron: $PbS + Fe = FeS + Pb$.

Lead obtained from the native ores contains varying quantities of antimony, tin, copper, silver, gold, etc. Much of the lead is worked for silver, and the desilverizing process removes nearly all the other metals, so that much of the commercial lead is chemically almost pure.

Physical Properties.—Lead is a bluish-white metal with bright metallic luster and specific gravity 11.37. It is soft enough to mark upon paper, to be impressed with the finger-nail, and to be cut with a knife. Its alloys with other metals are harder. Its tenacity, elasticity, and malleability are all low, but it may be rolled into thin sheets and drawn out into pipes. It melts at 325° and distils at about 1700°. It contracts on cooling, and its volume is diminished and density increased by pressure and hammering. It crystallizes from fusion in regular octahedrons, and when separated from its compounds frequently assumes arborescent crystalline forms.

Chemical Properties.—Lead tarnishes easily in the air, and becomes coated with the suboxid Pb_2O, which protects it from further oxidation. It burns when heated to PbO or Pb_3O_4. When finely divided it ignites spontaneously. It is insoluble in pure water, but in contact with air and water it forms lead hydroxid, PbH_2O_2, which is slightly soluble. If the water contains carbon dioxid together with mineral salts, such as phosphates, carbonates, and sulfates, the lead becomes covered with an insoluble coating of carbonate or sulfate of lead. When carbon dioxid is in excess some of the carbonate may go into solution. It is these properties which make lead-pipes dangerous when used for the domestic water-supply. It dissolves poorly in strong acids because of the formation of insoluble lead salts. Weak acids attack it more readily. It dissolves easily in nitric acid, forming lead nitrate, but no hydrogen, since this is oxidized by the decomposing nitric acid:

$$Pb + 4HNO_3 = 2NO_2 + 2H_2O + Pb(NO_3)_2.$$
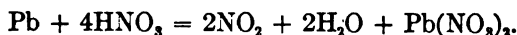
Zinc, tin, and iron precipitate it from its solutions.

Physiological Properties.—All the soluble salts of lead are cumulative poisons. When taken continuously in the smallest quantities the lead remains in the tissues until a sufficient amount has accumulated to produce the poisonous effects. When taken in

large doses it produces an acute colic. The cumulative effects are malaise, dyspepsia, and paralysis of the forearm.

Illustrations.—Cut a bar of lead with a knife and note its color and luster and see how rapidly it tarnishes.

To show the spontaneous combustion of lead, heat in a tube some lead tartrate until fumes no longer escape, cork tightly and let cool. On pouring the mixture of finely divided lead and carbon out into the air it falls in a brilliant shower of fire. To prepare the lead tartrate, add lead acetate to a solution of sodium potassium tartrate until precipitation is complete, then filter and dry the precipitate.

To show the displacement of lead by zinc, place a coiled strip of zinc in a solution of lead acetate. Beautiful arborescent crystals of lead grow out from the zinc. This is called the *lead tree.*

To obtain crystals melt the lead, allow it to cool until partially solidified, and pour off that which remains liquid. The vessel will be covered with octahedral crystals of lead.

Uses.—Lead is used chiefly for shot, lead-pipe, sheet lead, and in the manufacture of lead alloys and lead salts. For shot it is alloyed with about 2 per cent of arsenic. This hardens it and makes the shot assume the spherical form as they fall from the tower. In making lead-pipe semifluid lead is forced through steel dies. Sheet lead is used for lining the sulfuric-acid chambers and vats.

Alloys of Lead.—Lead is a constituent of solder, pewter, bronze, queen's metal, tin-foil, and terne-plate, all of which have been described under tin.

Type-metal is an alloy of lead, antimony, and tin in about the proportion 50, 25 and 25.

Babbit-metal is used as an antifriction lining for machinery bearings. Analysis of a sample gave lead 40, tin 45.5, antimony 13, copper 1.5.

Lead also forms alloys with bismuth, copper, mercury, potassium, sodium, palladium, platinum, zinc, chromium, and manganese.

LEAD COMPOUNDS.

Lead is metallic and strongly basic. Its principal ion is $\overset{+}{Pb}''$, and as a dyad it forms salts with most of the acids and unites to the negative elements generally. It still, however, retains a trace of acid character, since its oxids, PbO and PbO_2, unite to the alkali

hydroxids to form plumbites and plumbates. Lead does not unite to hydrogen.

The thermal equations for some of the more important compounds are:

(Pb,O) = 50,300 c.	(Pb,O$_2$) = 12,100 c.	(Pb, Cl$_2$) = 82,800 c.
(Pb,Br$_2$) = 64,400 c.	(Pb,I$_2$) = 39,600 c.	(Pb, S) = 20,400 c.
(Pb,S,O$_4$) = 216.200 c.	(Pb,N$_2$,O$_6$) = 105,500 c.	(Pb,C,O$_3$) = 72,900 c.

LEAD HALIDS.

Lead Fluorid, PbF$_2$, is a white powder obtained by heating lead oxid with hydrofluoric acid, or by treating a lead salt with a soluble fluorid.

Lead Chlorid, Plumbous Chlorid, PbCl$_2$, is formed by the action of chlorin upon lead. It is more easily prepared by treating the oxid or carbonate with hot hydrochloric acid. It is precipitated from strong solutions of lead salts by hydrochloric acid or soluble chlorids.

Lead chlorid is a white crystalline solid of specific gravity 5.8. It forms long silky rhombic needles soluble in 135 parts of cold water and in 30 parts of boiling water. It melts at 500° and volatilizes at a white heat.

Lead Oxychlorids.—When lead chlorid is heated in the air oxychlorids or basic chlorids are formed. Pb$_2$OCl$_2$ occurs as the mineral *matlockite.* Pb(HO)Cl is obtained by adding lime-water to a solution of lead chlorid, and is the pigment known as *Pattinson's white lead.* Other oxychlorids are PbCl$_2$,3PbO, *Turner's yellow,* and PbCl$_2$,7PbO, *Cassel yellow.*

Lead Chlorofluorid, PbClF, is a white precipitate obtained by boiling lead chlorid with a solution of potassium chlorid.

Plumbic Chlorid, PbCl$_4$, is obtained in solution by dissolving lead dioxid in cold hydrochloric acid. By adding ammonium chlorid to the solution, *ammonium plumbic chlorid,* PbCl$_4$,2NH$_4$Cl, is precipitated, from which the plumbic chlorid is separated by action of sulfuric acid. It is an oily yellow fuming liquid which is decomposed by water.

Lead Bromid, PbBr$_2$, is obtained by treating lead oxid with hydrobromic acid. It forms white shining needles of specific gravity 6.6. It melts at 500° and boils at 861°. When heated in the air it passes to the oxybromid, Pb$_2$OBr$_2$, a pearly yellow solid.

Lead Bromochlorid, PbBrCl, is a white crystalline solid.

Lead Iodid, PbI_2, is formed by dissolving lead in hydriodic acid, or by adding a soluble iodid to a solution of a lead salt. It dissolves in 194 parts of boiling water, and crystallizes from the solution in yellow gold-like leaves of specific gravity 6.1. Several *oxyiodids* are known. $Pb(HO)I$ is formed by adding potassium iodid to a solution of lead acetate.

Lead Iodochlorid, $PbICl$, and **Lead Iodobromid,** $PbIBr$, have been prepared.

Lead Cyanid, $PbCN$, is a white powder formed by the action of potassium cyanid upon lead salts.

OXIDS AND HYDROXIDS OF LEAD.

In addition to the regular plumbous and plumbic oxids, PbO and PbO_2, there are three other compounds of lead and oxygen, the suboxid, Pb_2O or $\begin{array}{c}Pb\\ |\\ Pb\end{array}\Big\rangle O$, and two mixed compounds, lead trioxid or metaplumbous plumbate, Pb_2O_3 or $Pb''Pb^{IV}O_3$ or $Pb<^O_O>Pb = 0$, and lead tetroxid or orthoplumbous plumbate, Pb_3O_4 or $Pb_2''Pb^{IV}O_4$ or $Pb<^O_O>Pb<^O_O>Pb.$

Lead Suboxid, Pb_2O, is a black, velvety powder obtained by gently heating lead oxalate. It is decomposed by heat into lead and lead oxid and burns in the air to lead oxid. This is the oxid formed upon the surface of lead when it tarnishes in the air.

Plumbous Oxid, or simply **Lead Oxide,** PbO, is formed when lead, its nitrate, carbonate, or other oxids are heated in the air. It is a yellow powder known in commerce as *massicot,* and the native mineral bears the same name. When cooled from fusion it forms a reddish crystalline scaly mass called *litharge.*

Lead oxid is slightly soluble in water (1 part to 7000), forming an alkaline solution. It dissolves in acids, yielding plumbous salts, and is thus strongly basic. With the alkali hydroxids it has a feebly acid action, forming plumbites, as K_2PbO_2. It saponifies fat, making *lead soap.*

This compound is largely used in the manufacture of flint glass and red lead and the various lead salts. It is employed as a glaze for earthenware, on the surface of which it forms a glassy lead silicate impervious to water.

Lead Hydroxid, or **Plumbous Hydroxid,** PbH_2O_2, separates as a white precipitate when a base acts upon a solution of a lead salt. Its chemical actions are like those of lead oxid. The hot aqueous solution deposits lead oxid on cooling.

Basic Lead Hydroxids are formed when alkalies act upon solutions of basic lead salts. The two most important ones are PbO,PbH_2O_2 or $HO—Pb—O—Pb—OH$ and $2PbO,PbH_2O_2$ or $HO—Pb—O—Pb—O—Pb—OH$.

Plumbic Oxid (Lead Dioxid), PbO_2, is obtained by treating red lead, Pb_3O_4, with nitric acid:

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + 2H_2O + PbO_2.$$
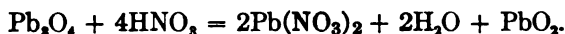
It is a light-brown powder, which is unstable and a powerful oxidizer. With acids it forms plumbous salts, and with strong alkalies it forms plumbates.

Plumbic Acid and Plumbates.—Neither the orthoplumbic acid, H_4PbO_4, nor the meta, H_2PbO_3, has been isolated, but they are represented in their salts. When lead is exposed to moist air, lead hydroxid and hydrogen peroxid are formed, but it is probable that the first result of the reaction is orthoplumbic acid:

$$Pb + 2H_2O + O_2 = H_4PbO_4,$$
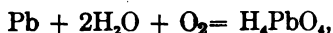
which at once decomposes $H_4PbO_4 = PbH_2O_2 + H_2O_2$.

Lead Trioxid (Sesquioxid), Pb_2O_3, or PbO,PbO_2 or $Pb''Pb^{IV}O_3$, *lead metaplumbate,* is obtained by treating with sodium hypochlorite a solution of lead oxid in potassium hydroxid:

$$2PbO + NaClO = NaCl + Pb_2O_3.$$
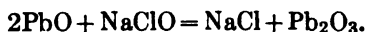
It is an orange-colored powder, which is decomposed by heat into oxygen and lead oxid, and by acids into plumbous and plumbic oxids, the former acting with the acid to give plumbous salts.

Lead Tetroxid, Red Lead, Minium, Plumbous Orthoplumbate, Pb_3O_4, or $Pb_2''Pb^{IV}O_4$, is prepared by heating lead carbonate or lead oxid to a temperature not exceeding 450°. It is a scarlet crystalline powder of specific gravity 8.6 to 9.1. Above 450° it gives up oxygen and returns to the lower oxid. It is decomposed by dilute acids into PbO_2 and PbO, the latter forming plumbous salts with the acid. With strong hydrochloric or sulphuric acid the lead salt is formed with the evolution of chlorin or oxygen. It is used as a pigment and in the manufacture of flint glass.

LEAD WITH SULFUR, SELENIUM, AND TELLURIUM.

Lead Sulfid, PbS, occurs native in very large quantities as the mineral *galena.* It forms cubical crystals having the color and luster of lead and a specific gravity 7.25 to 7.7. It is obtained artificially by the action of hydrogen sulfid upon lead salts, or by heating lead in sulfur vapor. It melts at red heat and sublimes *in vacuo,* condensing in cubes. Heated in the air it oxidizes to lead sulfate and lead oxid. It dissolves in hot hydrochloric acid, evolving hydrogen sulfid. · Dilute nitric acid converts it into the nitrate, while the strong acid oxidizes it to the sulfate.

Lead Sulfochlorids.—When hydrogen sulfid is passed into a solution of lead chlorid the precipitate is first yellow, then brown, and finally black. The colored precipitates consist of lead sulfochlorids, the chief of which are $PbS,PbCl_2$ and $3PbS,PbCl_2$.

Lead Selenid, PbSe, occurs native as the mineral *clausthalite,* found in the Hartz Mountains, in Spain, and in South America.

Lead Tellurid, PbTe, occurs as the mineral *altaite,* found in the Altai Mountains, and in Colorado, California, and Peru.

LEAD WITH THE NITROIDS.

Lead does not unite with nitrogen or phosphorus. It does not form definite compounds with arsenic, antimony, tin, or bismuth, but alloys with them in all proportions.

LEAD SALTS.

Lead forms numerous salts, both normal and basic, some soluble and some insoluble. The soluble salts have a sweet, astringent taste and are cumulative poisons. They precipitate, in acid solution with hydrogen sulfid, black-lead sulfid, with sulfuric acid white lead sulfate, with potassium chromate, yellow lead chromate. The binary salts of lead have already been described. The principal ternary salts are the chlorate, chlorite, bromate, iodate, sulfates, sulfites, thionate, thiosulfate, selenate, selenite, molybdates, tungstates, uranates, nitrates, nitrites, phosphates, phosphites, hypophosphite, arsenate, arsenite, antimonate, vanadate, carbonates, thiocarbonate, silicates, borates.

Lead Sulfate, $PbSO_4$. occurs native as the mineral *anglesite* in white rhombic crystals of specific gravity 6.2. It is obtained as a

white precipitate by treating a lead salt with sulfuric acid or a soluble sulfate. It melts at a red heat and is slightly soluble in water and dilute sulfuric acid. It dissolves readily in strong sulfuric acid, in hot hydrochloric acid, in alkalies, and in certain ammoniacal salts, especially the acetate. From solution in sulfuric acid it is deposited as the acid sulfate, $PbSO_4,H_2SO_4,H_2O$; and when it is treated with ammonia it is changed to the basic salt, $PbO,PbSO_4$, or $O<{Pb-O \atop Pb-O}>SO_2$. Both are white crystalline solids.   .

Lead Storage-battery.—If two plates of lead, one of which has been covered with plumbic oxid, be immersed in dilute sulfuric acid and connected by wires, an electric current is produced, the lead and the lead dioxid both being gradually changed into lead sulfate, which covers the plates. If now a current from a dynamo be passed through the system in the opposite direction, the chemical action is reversed and the sulfate becomes lead and lead dioxid again. Such a system is called a *storage-battery*. It may be exhausted and recharged an indefinite number of times.   .

Lead Chromate, $PbCrO_4$, occurs as the mineral *crocoïsite* in yellow monoclinic prisms of specific gravity 5.9 to 6.1. It is found in Siberia, Brazil, Hungary, and the Philippine Islands. It is precipitated from solution of lead salts by potassium dichromate. It melts easily, is decomposed at a high temperature, is insoluble in water and nitric acid. It dissolves in strong bases to a yellow solution, the lead becoming tetravalent and the solution probably containing potassium plumbate; or the cation Pb″ is oxidized to the anion $(PbO_2)''$. This action is general. All hydroxids which are both acidic and basic form difficultly soluble salts which are soluble in alkalis.   .

Lead chromate is used in the laboratory as an oxidizing agent, particularly in organic analysis, taking the place of copper oxid. It is used as a pigment under the name of *chrome yellow. Cologne yellow* is a mixture of lead chromate and lead sulfate.

Basic Lead Chromate, $PbO,PbCrO_4$ or $O<{Pb-O \atop Pb-O}>CrO_2$, is the *chrome red* of commerce. It is obtained by digesting chrome yellow with potassium hydroxid. *Chrome orange* is a mixture of chrome red and chrome yellow.

Lead Acetate, $Pb(C_2H_3O_2)_2,3H_2O$, or *sugar of lead,* is an organic salt, but its importance justifies its description here. It is the most used of all the lead compounds, since it is easily soluble, and the lead ion is freely separated in the solution. It is prepared by the action of acetic acid upon lead oxid. It is a white crystalline solid with sweet taste, melts in its water of crystallization, and loses the water at 100°. Carbon dioxid precipitates lead carbonate from solution of lead acetate, but the precipitation is not complete. The cloud which appears when it is dissolved in water is the carbonate and may be removed by adding a few drops of acetic acid.

Basic Lead Acetate, $(C_2H_3O_2)PbOH$, is obtained by dissolving lead oxid in a solution of lead acetate. The solution is called *lead vinegar* and is used in medicine and as a laboratory reagent. It contains free hydroxyl ions and colors litmus blue.

Lead Nitrate, $Pb(NO_3)_2$, is most readily obtained by dissolving lead oxid in nitric acid: $PbO + 2HNO_3 = H_2O + Pb(NO_3)_2$. It crystallizes in octahedrons of specific gravity 4.47. It dissolves in two parts of water and is decomposed by heat into PbO, NO_2 and oxygen. It is used in dyeing and calico printing and in the manufacture of chrome yellow.

Basic Lead Nitrate, $Pb(NO_3)OH$, separates in colorless crystals when a solution of lead nitrate is boiled with lead oxid. Several other basic lead nitrates having a larger proportion of PbO have been prepared.

Lead Phosphates.—The normal lead orthophosphate, $Pb_3(PO_4)_2$, is thrown down as a white precipitate when sodium phosphate is treated with lead acetate. Acid lead phosphate, $HPbPO_4$, is formed by the action of phosphoric acid upon lead nitrate. Lead forms several mixed phosphates, of which the mineral *pyromorphite* is an example., $Pb_3(PO_4)_2,Pb_2ClPO_4$.

Lead Carbonate, $PbCO_3$, occurs as the mineral *cerussite* in rhombic crystals of specific gravity 6.46. It is obtained by the action of ammonium carbonate or carbon dioxid upon solution of lead acetate. It is scarcely soluble in water, but dissolves more readily in water containing carbon dioxid or ammonium salts.

Basic Lead Carbonates.—Lead has a strong tendency to form basic carbonates. Alkali carbonates precipitate them from lead nitrate solution. They are also formed by the action of carbon dioxid upon lead oxid. The action is slow, and acetic acid is used

as a catalytic agent to hasten it, since lead acetate is more easily changed than lead oxid.

The most important of the basic carbonates is that known as *white lead.* This is a mixture in which $2PbCO_3,Pb(HO)_2$ predominates. The structure of this compound may be expressed thus: HO—Pb—O—CO—O—Pb—O—CO—O—Pb—OH.

White lead is a heavy amorphous powder, very opaque and insoluble in water. Its principal use is as a pigment, and for this purpose it has no superior. It gradually darkens because of the action of the hydrogen sulfid of the air, and hence does not make a permanent white. To disguise this change lead paint is generally tinted with light colors.

Manufacture of White Lead.—Of the various methods of preparing white lead, the oldest and best is that known as the *Dutch method.* Lead in thin sheets is placed in pots, the bottoms of which are covered with acetic acid not in contact with the lead. The pots are placed in heaps, each tier being separated from the others by boards and a layer of spent tanbark, the whole completely filling the room which contains it. The fermentation of the tanbark produces heat and carbon dioxid. The acetic acid is vaporized by the heat and converts the lead into basic lead acetate:

$$2H(C_2H_3O_2) + 2Pb + O_2 = Pb(C_2H_3O_2)_2, PbH_2O_2.$$
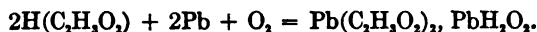
The basic acetate is decomposed by the carbon dioxid with the formation of acetic acid and white lead:

$$2(Pb(C_2H_3O_2)_2,PbH_2O_2) + CO_2 + H_2O = 4C_2H_4O_2 + 2PbCO_3,PbH_2O_2.$$
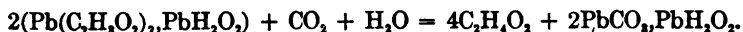
Thus the acetic acid is used over and over. The process is slow, lasting for three or four months. When the action is complete the white lead is removed, washed free from acetic acid, ground fine, and sent into the trade either dry or mixed with about 10 per cent of raw linseed oil.

In the *Thénard* or *French process*, the basic acetate is obtained by boiling lead oxid with lead acetate and then decomposing with carbon dioxid.

In the *Milner process*, lead oxid, sodium chlorid, and water are ground together, whereby a lead oxychlorid is formed, and this is decomposed with carbon dioxid.

Lead Silicate.—Lead oxid and silicic oxid melt together to a yellow glass, which is no doubt lead silicate, though no definite compound has been separated. It is a constituent of flint glass.

CHAPTER XXIX.

GROUP IV A. THE TITANOIDS. TITANIUM GROUP.

Titanium 48.   Zirconium 90.   Cerium 140.   Thorium 232.

THE elements of this group bear a close resemblance in many respects to carbon and silicon.   They are on the whole more metallic and less negative, though all but thorium form acids.   The principal valence is four, but they act often with the valence two, and sometimes with the valence three.   They all form dioxids, tetrahalids, ortho and meta hydroxids, and with the exception of cerium, fluo salts.

TITANIUM.

Symbol Ti.   Atomic weight 48.   Valence II and IV.   Specific gravity 3.6.

Occurrence.—Titanium does not occur free on the earth, but is a constituent of the solar atmosphere.   Combined it is widely distributed, being found in most rocks and in the bodies of many plants and animals. Titanic iron ore contains ferrous titanate, $FeTiO_3$.

History.—Titanium was first recognized as a distinct metal by William McGregor in 1791.   It was further investigated by Klaproth in 1795, who named it after the god Titan, one of the seven sons of Uranus and Gea.   The oxid was obtained pure by Rose in 1821.

Preparation.—Titanium may be obtained by heating in a covered crucible a mixture of potassium and potassium fluotitanate, and dissolving out the potassium fluorid with water.   Thus prepared, it is contaminated with titanium nitrid.   The pure metal is obtained by heating potassium fluotitanate in the vapor of sodium.

Properties.—Titanium is a dark-gray amorphous powder resembling reduced iron.   It has specific gravity 4.8, and when compact has a metallic luster.   It dissolves in boiling water and warm dilute acids with evolution of hydrogen.   It burns brightly when heated in the air, forming the oxid and nitrid, and when heated in oxygen burns with explosive violence.

446

COMPOUNDS OF TITANIUM.

Titanium forms numerous compounds quite analogous to those of silicon. The usual valence is IV, but in some compounds it is II, and in others apparently III.

Titanium Fluorid, TiF_4, is a fuming colorless liquid obtained by heating with sulfuric acid in a platinum vessel a mixture of calcium fluorid and titanic oxid.

Fluotitanic acid, H_2TiF_6, is a syrupy liquid obtained by dissolving titanic oxid in hydrofluoric acid. The fluotitanates are isomorphous with the fluosilicates.

Titanous Chlorid, $TiCl_2$, is a light-brown inflammable powder obtained by passing dry hydrogen over heated $TiCl_4$.

Titanium Sesquichlorid, Ti_2Cl_6, is obtained in violet scales by heating a mixture of titanic chlorid and hydrogen.

Titanic Chlorid, $TiCl_4$, is formed by direct union when titanium is heated in chlorin, or by heating a mixture of titanic oxid and carbon in chlorin. It is a colorless, fuming, mobile liquid of specific gravity 1.76 and boiling-point 135°. There are several *oxychlorids*, of which $Ti_2O_3Cl_2$ is an example.

Titanic Bromid, $TiBr_4$, is obtained by heating a mixture of titanic oxid and carbon in bromin vapor. It is a yellow crystalline solid with specific gravity 2.6, melting-point 39°, and boiling-point 230°.

Titanic Iodid, TiI_4, is obtained by heating titanium in iodin vapor. It is a reddish-brown, fuming, brittle solid which melts at 150° and distils at 360°.

Titanium Sulfid, TiS_2, is prepared by passing vapor of carbon disulfid over heated titanic oxid. It forms yellow scales resembling mosaic gold.

Titanium Nitrids.—Titanium is one of the few elements that combine directly with nitrogen. There seems to be several compounds, of which TiN_2 and Ti_3N_4 are the most important. They are red or yellow metal-like crystalline solids.

Titanic Oxid, TiO_2, occurs as three distinct minerals, *rutile, octa-hedrite* (anatase), and *brookite*. Rutile crystallizes in modified square prisms and pyramids of reddish color and specific gravity 4.25. Octahedrite crystallizes in square octahedrons of brown color and specific gravity about 3.9. Brookite crystallizes in rhombic prisms, brown, yellow, or black, and of specific gravity about 4.2.

Titanium Sesquioxid, Ti_2O_3, is a black solid obtained by heating the dioxid in a current of hydrogen.

Orthotitanic Acid, H_4TiO_4, is obtained by treating the hydrochloric-acid solution of titanium with an alkaline hydroxid. It is a white powder easily soluble in acids.

Metatitanic Acid, H_2TiO_3, is prepared by boiling acid solutions of titanic oxid, or by oxidizing titanium with nitric acid, or by heating the ortho acid to 140°. It is a soft white powder insoluble in water.

Titanium Salts.—Titanium forms a few salts corresponding to the two oxids. In addition to these there are titanyl salts containing the radical (TiO)″. An example is titanyl sulfate (TiO)SO₄.

<h2 style="text-align:center">ZIRCONIUM.</h2>

Symbol Zr. Atomic weight 90. Valence II and IV. Specific gravity 4.15. Melting-point 1500°.

Occurrence.—The principal native compound of zirconium is the mineral zircon, which is essentially *zirconium silicate*, $ZrSiO_4$. The gems *hyacinth* and *jargon* have the same composition.

History.—In 1789 Klaproth discovered a new earth in zircon and called it *zirconia*. The element was first isolated by Berzelius, and crystallized zirconium was first obtained by Troust. The name is probably Persian and means *gold-colored*.

Preparation.—Zirconium is prepared by heating a mixture of potassium fluozirconate and potassium, and dissolving away the potassium fluorid with water, or by passing the vapor of zirconium chlorid over ignited sodium.

Properties.—Zirconium is a gray, metallic powder which may also be obtained in crystalline scales of specific gravity 4.15. It burns in the air and is not attacked by acids, except hydrofluoric. It melts at about 1500°.

<h3 style="text-align:center">ZIRCONIUM COMPOUNDS.</h3>

The compounds of zirconium are analogous to those of titanium, though less easily formed and less numerous. Zirconium is both basic and acidic, the basic character being a little more marked than in the case of titanium.

Zirconium Fluorid, ZrF_4, obtained by heating zirconium oxid with ammonium fluorid, crystallizes in triclinic prisms of composition $ZrF_4,3H_2O$.

Fluozirconates.—There is a series of fluozirconates, of which the most important is K_2ZrF_6.

Zirconium Chlorid, $ZrCl_4$, is a white powder obtained by igniting in chlorin a mixture of zirconium oxid and carbon. It dissolves in water, forming the oxychlorid $ZrOCl_2$.

Zirconium Bromid, $ZrBr_4$, is a white crystalline powder obtained by igniting zirconium oxid and carbon in bromin. It absorbs moisture from the air to form the oxybromid $ZrOBr_2$.

Zirconium Oxid, ZrO_2, is produced by the combustion of the amor

phous metal. It is a white tasteless powder, or hard, transparent, quadratic crystals, insoluble except in strong sulfuric and hydrofluoric acids.

Orthozirconic Acid, H_4ZrO_4, and Metazirconic Acid, H_2ZrO_3, have been separated and are represented in various zirconates.

Zirconium Salts.—Zirconium forms chiefly zirconic salts, of which examples are *zirconium sulfate*, $Zr(SO_4)_2$, *zirconium nitrate*, $Zr(NO_3)_4$, and *zirconium silicate*, $ZrSiO_4$. The last is found in the native mineral *zircon*, which crystallizes in square prisms and pyramids.

Zirconium also forms compounds with sulfur, nitrogen, and carbon.

<center>CERIUM.</center>

Symbol Ce. Atomic weight 140. Valence III and IV. Specific gravity 6.7. Melting-point 800°.

Occurrence.—Cerium occurs as a small constituent of many minerals, usually associated with lanthanum, iron, and aluminum. Its principal ore is the mineral *cerite*, which is a more or less impure cerium silicate, $CeSiO_4$. The chief locality is Sweden.

History.—In 1803 Klaproth separated a new earth from a Swedish mineral. It was called *cerium*, from the planet *Ceres*, which had just been discovered. The metal was first prepared by Mosander in 1826.

Preparation.—Cerium may be prepared from the chlorid by electrolysis or by heating it with sodium.

Properties.—Cerium is a steel-gray metal, lustrous, ductile, and malleable, and of specific gravity 6.6 to 6.7. It tarnishes in moist air, melts at 800°, and burns to CeO_2. It also burns in chlorin and bromin and in the vapors of iodin, sulfur, and phosphorus. It decomposes water and dissolves in dilute acids.

<center>CERIUM COMPOUNDS.</center>

Cerium is decidedly basic, possessing little or no acidic character. It forms two series of compounds called *cerous* and *ceric*. In the former it seems to be trivalent, while in the second it is tetravalent. We can make but brief mention of the more important compounds.

Cerous Oxid, Ce_2O_3, is a green powder obtained by heating the oxalate or carbonate in hydrogen.

Ceric Oxid, CeO_2, is a pale-yellow powder obtained by heating several of the cerium salts.

Cerium Hydroxids.—The two hydroxids, CeH_3O_3 and $CeO(HO)_2$, have been prepared, but do not seem to possess marked acidic characters.

Halids and Salts.—Cerium forms cerous and ceric halids and salts.

THORIUM.

Symbol Th. Atomic weight 232.5. Valence II and IV. Specific gravity 11.

Occurrence.—Thorium occurs in small quantities in a number of rare minerals. Its principal ores are *thorite, orangeite,* and *monazite,* all of which are compounds of thorium along with various other metals.

History.—In 1828 Berzelius discovered a new earth in a rare mineral from Norway and named it *thoria,* after the Scandinavian god *Thor.* He separated the metal at the same time.

Preparation.—Thorium is prepared by heating the chlorid with sodium or potassium.

Properties.—Thorium is a gray powder, amorphous or crystalline, of specific gravity 11 and specific heat 0.0267. It burns brilliantly in the air to ThO_2 and in sulfur vapor to ThS_2. It dissolves readily in nitric acid.

COMPOUNDS OF THORIUM.

Thorium, like cerium, is almost destitute of acidic properties and acts generally with the valence four. It forms oxid, hydroxid, halids, and salts. Its compounds exhibit a radioactivity which is attributed to the hypothetical element actinium.

Thorium Sulfate, $Th(SO_4)_2$, obtained by dissolving thorium oxid in sulfuric acid, crystallizes with varying quantities of water according to the temperature.

Thorium Nitrate, $Th(NO_3)_4,6H_2O$, is a very soluble salt obtained by dissolving thorium oxid in nitric acid. It is used in the preparation of mantles for incandescent gas burners. The mantles made of cotton thread are dipped in a solution of thorium nitrate and dried. On being ignited, the thread burns away, leaving a coherent framework of thorium oxid. When this is rendered incandescent by a Bunsen flame, it emits a bright white light. The addition of one per cent of cerium oxid renders the mantle more powerfully luminous.

Note.—Professor Charles Baskerville, lately of the University of North Carolina, now of the College of the City of New York, has recently published the results of investigations which lead him to the conclusion that thorium is a complex substance with at least three constituents. Retaining the name Thorium for the one, he suggests for the other two Berzelium, for Berzelius, the discoverer of thorium, and Carolinium, for the Carolinas, where the thorium ores are found. The provisional atomic weights are Cn 212, Tr 220, and Bz 256.

CHAPTER XXX.

THE ATMOSPHERE.

Definition.—The term *atmosphere* (Greek, *vapor - sphere*) is applied to the gaseous envelope which surrounds the earth. The term *air* (Greek, *aer*) indicates any portion of the atmosphere. We say a vessel is filled with air, not with atmosphere. The older chemists, used the word air in the sense in which we use the word gas. Hydrogen was inflammable air; ammonia, alkaline air; carbon dioxid, fixed air; oxygen, dephlogisticated air.

Occurrence and Limits.—The air surrounds the earth, penetrates rocks and soils, and descends toward the earth's center as far as cracks and crevices permit. Upwards the air diminishes rapidly in density so that one half of it by weight lies within three and a half miles, and three fourths of it within seven miles of the surface. At the height of fifty miles it has become so rare as not to affect light rays, but meteoric and electric phenomena show its presence at a distance of 200 miles from the surface of the earth.

History.—Accurate investigation of the properties of the atmosphere began with Torricelli, who in 1643 showed that the air had weight and that the mercury column in the barometer is supported by atmospheric pressure. Lavoisier showed in 1772 that combustion was supported by some constituent of the air, and in 1775 proved this to be oxygen. Cavendish in 1781 found the main constituents to be oxygen and nitrogen. Carbon dioxid and water were early recognized, and since 1894 five other gases have been discovered in the atmosphere: viz., helium, neon, argon, krypton, and xenon. Other early investigators of the atmosphere were Priestley, Boyle, Bunsen, Stahl, Regnault, Pascal, Prout, Gay-Lussac, Thénard, Brunner, Humboldt, Davy, Dumas, Bousingault, Angus Smith, and many others.

451

Air a Mixture.—That the constituents of the air are simply mixed, and not chemically combined, is proved by the following considerations:

1. They do not occur in atomic proportions.

2. A mixture of nitrogen and oxygen in the same proportion exhibits the properties of air.

3. When such a mixture is made there is no evidence of chemical action, such as heat, change of volume, etc.

4. The gases dissolve independently and in different quantities in water.

5. When air diffuses through a porous partition the nitrogen passes more rapidly than the oxygen.

6. The oxygen may be removed by oxidizing agents, leaving the nitrogen.

7. We are familiar with the compounds of nitrogen with oxygen, and their properties are not those of the air.

Composition of Air.—The composition of the air varies slightly with locality, season, latitude, and elevation. Being a mixture its constituents are liable to local variations, and it receives all sorts of impurities—solid, liquid, and gaseous.

Air is primarily and mainly composed of nitrogen, oxygen, argon, carbon dioxid, and water vapor. In proportion the first three are almost invariable, the fourth varies slightly, and the last varies within rather large limits. The following may be taken as the average composition of dry air:

	BY VOLUME.	BY WEIGHT.
Nitrogen	78.4 per cent.	75.95 per cent.
Oxygen	20.94 "	23.10 "
Argon	.63 "	.90 "
Carbon dioxid	.03 "	.05 "

To these must be added the moisture which is uniformly present, and quantities scarcely weighable of helium, neon, krypton, and xenon. Further, there are almost always present traces of ozone, ammonia, and nitric acid, besides the numerous impurities.

Nitrogen constitutes a little more than three fourths of the atmosphere, and the absolute quantity remains almost unchanged. It takes no part in chemical processes, but serves to dilute the oxygen and make it less active. It is oxidized in very small quantities by active combustion, by the lightning-stroke, and by ozone.

Oxygen is the active element in the air of which it composes

nearly one fourth. It supports life, combustion, and oxidation, and
is thus constantly being consumed; but it is set free again in various
native chemical processes, notably in the leaves of plants, so that
the proportion in the air remains about the same from year to year.

Argon constitutes a little less than one per cent of the air, and,
like nitrogen, is wholly inert. The other recently discovered gases
are present in quantities too small to be noticeable.

Carbon dioxid is an important constituent of the air, although its
proportion is less than one twentieth of one per cent. Its sources
are combustion, respiration, fermentation, and decay. It is washed
out by rains and is absorbed by the leaves of plants to be used in
starch-making. The production and consumption balance one
another so that the quantity remains almost unchanged.

Water is the most variable constituent of the atmosphere. When
the air contains all it will hold it is said to be *saturated*, or at the *dew-
point*. When the temperature of saturated air is lowered the water
condenses in the form of mist, rain, or dew. Air is said to be damp
or dry according to its nearness to saturation. The quantity of
water is indicated in a rough way by hygrometers, and may be
accurately determined by passing a measured volume of air through
a drying-tube and noting the tube's increase in weight.

The quantity of water which is required to saturate one cubic
meter of air at various temperatures is as follows:

At $-10°$ 2.28 grams. At $10°$ 9.36 grams. At $30°$ 30.10 grams.
At $0°$ 4.87 grams. At $20°$ 17.16 grams. At $100°$ 588.73 grams.

One cubic mile of air saturated at $35°$ will deposit 140,000 tons
of water when cooled to $0°$.

Ozone is formed by processes of decay, evaporation, slow com-
bustion, and electric action. It is consumed again in the oxidation
of organic matters and is therefore a purifying agent. It is most
abundant in country and mountain air and on the sea. Hydrogen
peroxid is also present in the moisture of the air and some of the
effects usually attributed to ozone are probably due to it.

Ammonia is almost uniformly found in traces in the air. It
results from organic decompositions and is removed by ozone and
water.

Nitric acid occurs in the air in traces mainly as nitrates. It is
due to the oxidation of nitrogen, is washed out by the rains, and
furnishes food to the plants.

Impurities.—The air is liable at all times to be contaminated. A common impurity is gases which result from the decay of organic matters. These are mostly ammonium and sulfur compounds, and to them bad odors are usually due. The vapors of volatile liquids, dust, organic and inorganic, bacteria and disease germs are lifted by the winds and float in the air everywhere.

The air purifies itself, and the safest sanitary means are those which prevent contamination rather than those which look to purification.

Analysis of Air.—The determination of the relative amounts of the two main constituents of the air has engaged the attention of many chemists. Two methods have been used. The first is called *eudiometry*, or *measure of goodness*. The opinion was that the amount of oxygen varied, and, as it was the supporter of life, that its measure was the measure of the goodness of the air. A graduated eudiometer tube is filled with air over water and the volume noted. Nitrogen dioxid is added until the oxygen is all removed and the residual volume is measured as nitrogen, while the decrease in volume represents the oxygen. Instead of N_2O_2 hydrogen may be used. A quantity of air is introduced into a bent eudiometer tube filled with mercury (Fig. 58). The mercury is brought to the same level in the two arms of the tube and the volume read. An excess of hydrogen is now introduced and the volume again read. The hydrogen and oxygen are made to unite by a spark from a Ruhmkof coil. The loss in volume is three times the volume of the oxygen in the air used. Correction must, of course, be made for temperature, pressure, and vapor tension of water. According to these determinations,

Fig. 58.

average air contains by volume: Oxygen 20.96 parts, and nitrogen and other gases 79.04 parts.

The second and more accurate method is that of Dumas and Bousingault. Air from which water and carbon dioxid have been removed is drawn over heated copper into a vacuous globe. The increase in weight of the copper is the amount of oxygen which was mixed with the amount of nitrogen represented by the increase in weight of the globe. Air was thus found to contain by weight: Oxygen 23 parts, and nitrogen and other gases 77 parts.

Argon may be separated from the air by processes which have already been described.

The presence of carbon dioxid is shown by the precipitate of calcium carbonate formed when air is drawn through lime-water. The quantitative determination is made by drawing a given volume of dried air through a potash bulb and noting the bulb's increase in weight.

Moisture is shown by cooling air. The dew on a vessel of ice-water is an illustration. It is quantitatively determined by drawing a measured volume through a desiccating-tube and noting the tube's increase in weight.

Ammonia and ammonium compounds are shown by the yellow color, or precipitate, caused when air is drawn through Nessler's solution.

Sulfur compounds blacken paper moistened with solution of lead acetate.

Dust and other solid particles are made visible when a beam of electric or calcium light is passed through the air.

Physical Properties of Air.—Air has the ordinary physical properties of its gaseous constituents. It is a bad conductor of heat and electricity when dry, better when moist. A liter weighs under standard conditions 1.293 grams. Its average pressure at sea-level is 760 millimeters of mercury. It is transparent and colorless, but when seen through great depths has a blue or gray color, due to the interference of suspended solid particles with light. It is very movable, and changes of temperature, causing changes of density, produce currents which appear as winds, storms, cyclones, etc.

At low temperatures air becomes a liquid mixture of nitrogen and oxygen, carbon dioxid and argon separating as solids. On standing liquid air loses nitrogen more rapidly than oxygen until the residue contains 93 per cent of oxygen and boils at −183°. Liquid air is therefore practically liquid oxygen and has a bluish color. In ordinary vessels it boils away rapidly, but in vacuum-jacketed flasks it remains quiet, evaporating slowly. Two liters may be thus kept for ten or fifteen days, losing only about 100 cc. a day.

Chemical Properties of Air.—The active element in the air is oxygen, and its chemical properties are those of this gas moderated in degree by its dilution with nitrogen. Its chemical actions are greatly assisted by the presence of moisture, hydrogen peroxid, and ozone.

Liquid Air.—Lindé's apparatus for liquefying air consists essentially of a pump (*P*), a cooler (*J*), a double spiral tube surrounded with non-conducting material (*D*), and a reservoir for the liquid (*T*). The double tube, which is several hundred feet long, is so arranged that the air in

the inner tube is subjected to a pressure of 200 atmospheres, while the pressure in the outer tube is only 20. The pump draws air from the outer and forces it into the inner tube. The air passes through the cooler to remove the heat due to compression, and is then allowed to flow through a cock (*R*) into the reservoir, where it is cooled by its sudden release from pressure and its rapid expansion. In a little while the air reaches the liquefying temperature and slowly collects in the receiver,

FIG. 69.—LINDÉ'S APPARATUS FOR LIQUEFYING AIR. (From the *Scientific American*, by permission.)

from which it may be drawn through the faucet (*V*). More air is admitted under pressure as it is required. The cloudy liquid is filtered from the frozen carbon dioxid and argon.

Illustrations.—Many curious and interesting experiments may be made with liquid air. Immersed in it, rubber becomes brittle, lead sonorous; a glowing splinter bursts into flame, notwithstanding the low temperature; mercury, ether, alcohol, and carbon dioxid are quickly frozen. If a vessel of it be placed on a block of ice the liquid boils away rapidly. Immerse in the liquid a wire or tube through which city gas is passing to a burner and the color of the flame gradually fades, because all the gases except hydrogen have been frozen in the tube.

Much has been said about the applications of liquid air in the arts, but so far its use is mainly limited to the securing of low temperatures for scientific purposes.

Uses of Air.—The uses of the air are manifold. It supports life and combustion, conveys moisture from sea to land, and deposits it

as rain. It finds many minor applications as a mechanical agent in the arts.

Ventilation.—Air is liable to be contaminated with the gases which come from fires, from the body, from the lungs, and from the walls of houses. Air that has been once breathed is not fit to be breathed again, and will scarcely support combustion. Its content has been reduced in oxygen and increased in carbon dioxid about 4.5 per cent, and besides it contains organic matters from the lungs, mouth, teeth, etc. It is necessary, therefore, to secure systematic ventilation of rooms occupied by man. This is usually effected by taking advantage of the change of density caused by change of temperature. The chimney not only carries off the products of combustion, but also removes bad air and draws in fresh air. A most excellent ventilating agent is the wind. An open window on the leeward side of the house causes a free circulation of air without hurtful currents.

Illustration.—Displace the water from a cylinder on the water cistern with air from the lungs, remove the cylinder quickly and insert a lighted taper. The flame is extinguished.

CHAPTER XXXI.

COMBUSTION.

History.—Fire was known to prehistoric man and charcoal is associated with his early remains. In ancient days fire became the center around which gathered the nation, the tribe, and the family. It was an object of worship and the sacred fire was kept at the public expense. The temple of Vesta had no image, since the fire was regarded as the goddess herself.

The true nature of combustion was not known until the discovery of oxygen by Priestley in 1775. From the seventeenth century up to that time the phlogiston theory had prevailed. A combustible was supposed to be a compound of some element with a substance called *phlogiston*, which in the process of combustion escaped, leaving the pure element in the form of a *calx*. On heating the calx with a substance rich in phlogiston the original substance was obtained. After the discovery of oxygen it was proven by the investigations of Stahl, Scheele, and others that (1) oxygen accelerates combustion and (2) the calx is heavier than the substance from which it is obtained. These discoveries caused the overthrow of the phlogiston theory.

Definition.—Combustion may be defined in general as *a rapid chemical action accompanied by light and heat.* In the ordinary and limited sense it means union with oxygen.

The *combustible* is that which burns. It may be solid, liquid, or gas. Examples are coal, wood, rock-oil, alcohol, city gas, hydrogen. The ordinary combustibles are organic matters.

The *supporter of combustion* is that with which the combustible unites, and is ordinarily oxygen gas. It may, however, be a liquid or a solid. When heated charcoal burns upon fuming nitric acid the acid is the supporter of combustion, since it supplies the oxygen.

458

So also two solids, as phosphorus and iodin, may burn together, and here either is the combustible or the supporter of combustion. When a jet of gas burns in air the gas is the combustible, but a jet of air burns equally well in an atmosphere of the gas.

Illustration.—Let city gas flow from a funnel-shaped glass tube inclined downward. Ignite the escaping gas and pass into it a jet of air or oxygen. The jet continues to burn.

Kindling Temperature.—It is a matter of ordinary observation that most bodies must be heated before they will take fire. The point at which the rapid combustion sets in is called the *kindling temperature*, or temperature of ignition. Phosphorus ignites at 40°, carbon disulfid at 149°, sulfur at 260°, wood, coal, gas, and the ordinary combustibles at red heat. Combustion will continue only when the heat of the action is sufficient to keep the burning body above the kindling temperature.

A flame will not pass through a small aperture or a wire gauze because the temperature of the gas within the openings is below the igniting point. When the gauze, however, becomes red-hot it sets fire to the gas beyond. This is the principle of the Davy safety-lamp used by miners. The lamp is surrounded by a hood of fine wire gauze. When it comes within an atmosphere of explosive or inflammable gas, that within the hood explodes or burns, while that without does not ignite. The miner is thus warned of his dangerous situation and retires.

Illustration.—Bring down upon a gas-flame a wire gauze and note that flame does not pass through. Extinguish the flame and light it above the gauze; it does not burn below. Move the gauze upwards and the flame is extinguished.

Temperature of Combustion.—The temperature of combustion is usually considerably above the igniting-point and depends upon the rapidity of the action and the nature of the combustible. A few examples will illustrate :

Gas-flame, 1200°.   Hydrogen-flame, 2024°.
Bunsen-flame, 1300° to 1500°.   Oxyhydrogen-flame, 2844°.
Charcoal-fire, 1400° to 1600°.   Electric-furnace, above 3000°.
Blast-furnace, 1800°.

Heat of Combustion.—The heat of combustion depends upon the nature of the combustible and is independent of the rapidity of the action. A ton of coal yields the same quantity of heat whether

it burns in an hour or in a day. The heat of combustion of hydrogen is greater than that of any other substance.

Rapidity of Combustion.—The rapidity of combustion, and hence the temperature, depends upon the nature of the combustible and the supply of air or oxygen. The oxidation may take place so slowly as to evolve but little heat and no light. It is then called *slow combustion.* Examples are the slow oxidation of phosphorus, the rusting of iron, and the decay of organic matters. Sometimes by slow combustion the temperature of the mass is gradually raised until it reaches the kindling-point, when the body takes fire. This is called *spontaneous combustion* and is liable to occur in heaps of oily rags, wool, damp hay, etc.

The rapidity of combustion is increased by a more abundant supply of air, as in the blast flame, or by finely dividing the combustible. If a powdered solid be mixed with air it will burn rapidly, even explosively. Finely divided lead, iron, and other metals burn spontaneously. Liquid fuel is atomized in a blast of air.

Explosives.—These are of two kinds: (1) intimate mixtures of the combustible and the supporter of combustion; and (2) unstable chemical compounds, usually solid or liquid, which contain within the same molecule atoms which are rearranged in the explosion to form gaseous compounds. In either case, when the mass is ignited the action runs rapidly through it, producing suddenly a large volume of gas with explosive effect.

To the first class belong all explosive mixtures such as (1) combustible gases with air or oxygen; (2) combustible solids or liquids with oxidizing agents (gunpowder); (3) finely divided solids or liquids with air or oxygen. Flour dust in mills sometimes burns with terrific explosions, destroying the buildings.

To the second class belong such substances as nitrogen iodid, guncotton, and nitroglycerin (dynamite). Nitroglycerin, $C_3H_5(NO_3)_3$, is a liquid whose molecule contains carbon, hydrogen, and oxygen in about the proportion in which they unite to form carbon dioxid and water together with nitrogen, which is set free as a gas. Its high explosive character depends upon its rapid decomposition and the sudden formation of a very large volume of gas.

Products of Combustion.—The products of combustion are of two kinds, physical and chemical. The physical products are light

and heat. The light is mainly due to the incandescence of solid particles. The heat is due to the chemical action.

The chemical products of combustion are the oxids of those elements which are found in the combustible. Iron burns to iron oxid, lead to lead oxid, hydrogen to hydrogen oxid, hydrogen phosphid to phosphoric oxid and water, and carbon disulfid to carbon dioxid and sulfurous oxid. Most combustibles are compounds of carbon, hydrogen, and oxygen. They burn therefore to carbon dioxid and water, the oxygen simply taking part in the action. Alcohol, for example, burns as follows:

$$C_2H_6O + O_6 = 2CO_2 + 3H_2O.$$
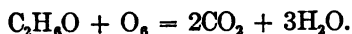
Since water and carbon dioxid are both colorless gases at the temperature of the combustion they pass away unseen and the substance is said to burn up or be destroyed. If these products are collected and weighed it will be found that there is no loss. Ash is composed of solid oxids and incombustible mineral matters.

Flame is produced by burning gas. If a body is not gaseous and not volatile it burns without flame or simply glows, as in the case of iron, copper, and carbon. If a solid or liquid is volatile, or if an intermediate volatile product is formed, the combustion is accompanied by flame.

Color of Flame.—Each combustible substance gives a flame color which is more or less characteristic. The flame of hydrogen is colorless, that of compounds of carbon and hydrogen is yellow, sulfur and carbon monoxid blue, cyanogen peach-blossom, phosphorus yellow. Metals burn with and impart to flames characteristic colors: sodium yellow, potassium violet, barium green, strontium crimson, copper green, iron red.

Luminosity of Flames.—The luminosity of flames seems to be mainly due to the presence of heated solid particles. It is also dependent upon temperature and pressure, increase of either of which makes the flame brighter. In a few luminous flames there seems to be no solid matter, as when phosphorus or arsenic burns in oxygen.

The luminosity of flames is increased (1) by increase of density of the gas; (2) by elevation of temperature; (3) by introduction of infusible solids.

1. In general the denser the gas the more luminous the flame. The flame of hydrogen is pale, that of acetylene very bright. Under pressure the hydrogen flame becomes luminous and the flames of other gases are made brighter.

2. When gases are heated before they enter the burner they emit more light. Substances burn in oxygen more brilliantly than in air because the temperature is higher.

3. The third principle is illustrated in the ordinary gas or candle-flame, in the lime-light, and in the Welsbach burner. The light of the candle-flame is mainly due to incandescent particles of carbon set free in the zone of incomplete combustion. In the lime-light the oxyhydrogen-flame plays upon a cylinder of lime, raising it to a white heat and making it brilliantly luminous. In the Welsbach burner a Bunsen-flame is surrounded with a mantle of infusible oxids of metals, chiefly thorium and cerium. The heated oxids emit a very bright and pure white light. To prepare the mantle, a mantle of cotton thread is immersed in a solution of the nitrates of the metals, then dried and burned, when a delicate, fragile skeleton of the metallic oxids remains. The electric-light is due mainly to the intensely white-hot carbon.

Structure of Flame.—The ordinary gas or candle flame has three parts:
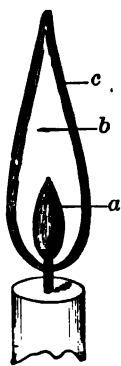
Fig. 70.

1. *The outer pale-blue envelope.*—This consists of gas in a state of complete combustion. It is scarcely luminous, because it is diluted and cooled by the influx of air and contains no free particles of carbon.

2. *The middle or luminous cone.*—This consists of gas in rapid combustion at a high temperature, but with an insufficient supply of air, so that a portion of the carbon remains for a time unburned and emits the light.

3. *The inner dark cone,* which consists of gas not yet ignited because it has not reached the kindling temperature or is not sufficiently mixed with air.

Illustrations.—Hold a match-stick across the flame so that it cuts the inner cone. It chars in two places, with an unburnt portion between.

Lower a sheet of paper well down into the flame and remove it before it ignites. The charred portion is in the form of a ring.

Insert the head of a match quickly into the inner cone. By a little dexterity the match may be removed with the head unburnt, after the portion of the stick which was in the outer flame is charred through.

Arrange an inclined glass tube so that its lower end is in the inner cone. The gas may be lighted at the upper end of the tube.

The Bunsen Flame.—In the Bunsen burner air is admitted below and thoroughly mixed with the gas in proper proportions, so that active combustion takes place throughout the whole flame, which is nearly non-luminous and has the character of the outer coat of the common flame. If too much air is admitted the mixture becomes explosive and the flame runs down to the base of the burner, when it must be extinguished and relighted.

The non-luminosity of the Bunsen flame is mainly due to the complete combustion and the dilution of the gas with the inert nitrogen; possibly also to the cooling effect of the air. Other gases, such as nitrogen, oxygen, and carbon dioxid, act in the same way as air.

The temperature of the Bunsen flame is higher than that of the luminous flame, though it is somewhat cooled below by the influx of air. The following temperatures were observed by Lewes, the burner consuming six cubic feet of gas per hour:
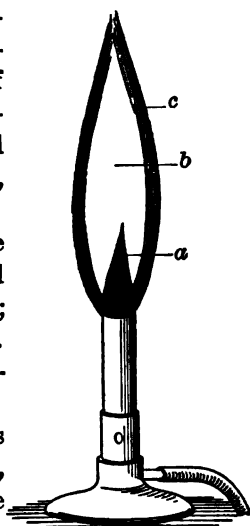
FIG. 71.

	Luminous flame.	Non-luminous flame.
One-half inch above burner..................	135°	54°
One and one half inch above burner	421°	175°
Tip of inner cone............................	913°	1090°
Center of outer cone	1328°	1533°
Tip of outer cone............................	728°	1175°

The *blast lamp* is similar to the Bunsen burner, but the action is intensified by a blast of air which secures complete and rapid combustion.

Oxidizing and Reducing Flames.—An *oxidizing flame* is one that contains an excess of oxygen, as the outer coat of all flames, luminous and non-luminous, and the main body of the Bunsen flame.

A *reducing flame* is one that is deficient in oxygen. It is generally more or less luminous. Examples are the luminous cone of flames in general and the portions of the Bunsen flame adjacent to the inner cone.

Illustration.—If a copper wire be held across the slightly luminous Bunsen-flame, just below the point of the inner cone, it will be seen to oxidize in the outer flame while it remains unchanged within. If the wire be slightly moved so as to bring the oxidized portion near to the inner cone the oxid will be reduced.

The Blowpipe.—The blowpipe introduces a current of air and serves the double purpose of directing the flame upon a small point and of raising its temperature. The mouth blowpipe is a bent tube of convenient length through which air is forced from the lungs. It is usually furnished with a chamber to catch the condensed moisture, and the point may be tipped with platinum to make it more durable. The blowpipe flame is somewhat like the Bunsen flame and has oxidizing and reducing regions. The hottest part is at the point of the inner cone, where a temperature of 2000° may be obtained. Beyond this point the action is oxidizing, while within the blue inner cone it is reducing.
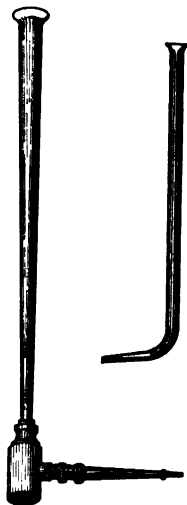
The blowpipe is suited to candle, gas, or alcohol flames. For use with gas a tube flattened and obliquely ground is introduced into a Bunsen burner and a small flame used.

Fig. 72.

The Electric Furnace.—For securing the highest temperatures the electric furnace is used. This consists essentially of two carbon electrodes meeting in a crucible of very refractory material such as graphite, lime, or magnesia, and the whole inclosed with a casing of firebrick. This furnace gives temperatures above 3000° and brings to fusion almost every known substance.

CHAPTER XXXII.

GROUP III B. THE BOROIDS. BORON GROUP.

Boron 11. Aluminum 27. Gallium 70. Indium 114. Terbium 160. Thallium 204.

OF the members of this group boron is almost wholly acidic, aluminum and gallium are both acidic and basic, indium is mainly basic and thallium is wholly basic. In boron we have the last of the really acidic elements. It possesses only traces of basic character, as seen in the binary salts and in a few compounds like boron phosphate, BPO_4. The valence of the group is three, but gallium, indium, and thallium exhibit other valences.

BORON.

Symbol B. Atomic weight 11. Valence III. Specific gravity 2.63.

Occurrence.—Boron does not occur free. Its principal compounds are *boric acid*, H_3BO_3, found in volcanic regions, *borax* or *tincal*, $Na_2B_4O_7,10H_2O$, *boracite*, $2Mg_3B_8O_{15},MgCl_2$, and *borocalcite*, $CaB_4O_7,4H_2O$.

History.—Boron was first prepared by Gay-Lussac and Thénard in 1808. The name is from borax, which is a Persian word.

Preparation.—Amorphous boron is obtained by heating with potassium boric oxid, potassium fluoborate, or boric chlorid.

Crystallized boron is obtained by igniting boric oxid with aluminum. The separated boron dissolves in the aluminum and on cooling crystallizes. When the aluminum is removed by hydrochloric acid the boron crystals remain.

Properties.—Boron presents two allotropic forms, the one amorphous, the other crystalline. Amorphous boron is a dark-green powder which burns in the air when strongly heated, uniting with both the oxygen and the nitrogen. It is oxidized by cold nitric or

warm sulfuric acid and acts with alkali salts to form borates. Crystallized boron forms monoclinic prisms and octahedrons which are inferior in hardness only to diamond. They have specific gravity 2.63, and are less easily acted upon chemically than amorphous boron. Boron volatilizes in the electric furnace without melting.

BORON COMPOUNDS.

Boron acts only with the valence III, forms but few binary compounds, and only boric and haloboric acids.

Hydrogen Borid, H_3B, is a very unstable compound which is obtained mixed with hydrogen by the action of hydrochloric acid upon magnesium borid, Mg_3B_2. It is a colorless gas which burns with a green flame to water and boric oxid. When passed through a heated tube boron is deposited.

Boron Fluorid, BF_3, is prepared by action of fluorin upon boron, or of hydrofluoric acid upon boric oxid, or by heating together boric oxid, calcium fluorid, and sulfuric acid:

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 2BF_3.$$
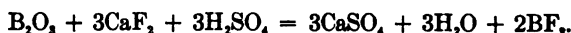
It is a colorless, fuming gas which neither burns nor supports combustion, but chars organic matters, because of its strong attraction for water. It is extremely soluble in water, one volume dissolving 1000 at $0°$. It unites with the water, forming boric and fluoboric acids:

$$4BF_3 + 3H_2O = H_3BO_3 + 3HBF_4.$$
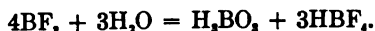
Fluoboric Acid, HBF_4, or $H-F=F-B\diagdown^F_F\vert$, is obtained by the reaction just given. It is a monobasic acid and yields metallic salts.

Boron Chlorid, BCl_3, is prepared by passing chlorin over heated boron, or a mixture of boric oxid and carbon:

$$B_2O_3 + 3C + 3Cl_2 = 3CO + 2BCl_3.$$
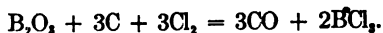
It is collected in a cooled receiver as a colorless, fuming liquid which boils at $18°$ and has specific gravity 1.35. It is decomposed by water thus: $BCl_3 + 3H_2O = H_3BO_3 + 3HCl$. It unites directly to ammonia to form $2BCl_3,3NH_3$.

Boron Bromid, BBr_3, is obtained by direct union, or by passing bromin over a heated mixture of boric oxid and carbon. It is a colorless, fuming liquid of specific gravity 2.69 and boiling-point $90°$. It acts toward water and ammonia as the chlorid does.

Boric Oxid, B_2O_3, the only oxid of boron, is formed when boron burns in the air. It is easily prepared by igniting boric acid. It is

a brittle glassy solid which absorbs moisture and becomes opaque.
At a red heat it converts the salts of volatile acid radicals into
borates:

$$B_2O_3 + 3Na_2SO_4 = 3SO_3 + 2Na_2BO_3.$$
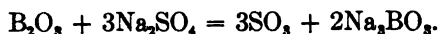
Its heat of formation is 317,200 calories.

Boric Acids.—Boric oxid unites to water to form three acids:

Orthoboric acid, H_3BO_3, $B(OH)_3$.
Metaboric acid, HBO_2, $H—O—B=O$.
Pyro or tetraboric acid, $H_2B_4O_7$, $H—O—B<^O_O>B—O—B<^O_O>B—O—H.$

Orthoboric Acid, H_3BO_3, is obtained by decomposing borax with
hydrochloric or sulfuric acid:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

The commercial acid is obtained mostly from the native compound, which occurs in solution in volcanic waters and as the mineral
sassolite. In the neighborhood of the fumaroles in Tuscany the
lagoons of water and the steam from the fumaroles contain boric
acid. The water is collected in cisterns, allowed to concentrate, and
finally evaporated in leaden pans until the boric acid crystallizes
out. The heat from the fumaroles is utilized in the process. The
acid is purified by recrystallization.

Boric acid is a soft white crystalline powder of specific gravity 1.4.
It dissolves in 24 parts water at 19° and in 3 parts at 100°. It is
more soluble in alcohol, and the solution burns with a green flame.
It is weakly acid and its salts are unstable.

Metaboric Acid, HBO_2, is obtained as a white powder by heating
the ortho acid to 100°.

Pyro or **Tetraboric Acid,** $H_2B_4O_7$, is obtained by heating the
ortho or meta acid to 160°. The meta and tetraborates are quite
stable salts.

Borates.—In addition to the ortho, meta, and tetraborates
there are other complex compounds containing more than four boron
atoms in the molecule. The most important of all the borates is
borax, $Na_2B_4O_7$, which will be described under sodium.

Boric Sulfid, B_2S_3, is formed by heating boron in sulfur vapor, or by
passing carbon disulfid over a heated mixture of boric oxid and carbon.
It is a white fusible solid which is decomposed by water into boric acid
and hydrogen sulfid. It has an unpleasant odor and hurts the eyes.

Boron Nitrid, BN, is a white amorphous powder formed by the union of boron and nitrogen at a red heat. It is infusible, insoluble in water, and not easily acted upon by chemical agents.

ALUMINUM.

Symbol Al. Atomic weight 27. Valence III. Specific gravity 2.58 to 2.68. Melting-point 700°.

Occurrence.—Aluminum does not exist free, and indeed is separated from its compounds with great difficulty. It is a constituent of many rocks and minerals, and is next to oxygen and silicon in abundance. It is found in all soils, but not in plants, except in certain cryptogams; and it exists in the solar atmosphere. Among the more important native compounds are the oxid, Al_2O_3, in corundum, sapphire, and ruby; hydroxids in diaspore, $AlO(HO)$, and bauxite, $Al_2Fe_2H_4O_5$; a fluoaluminate in cryolite, Na_3AlF_6; aluminates in spinel, $MgAl_2O_4$, and gahnite, $ZnAl_2O_4$; and a large number of silicates in which aluminum enters as one of the positive elements, as feldspar, mica, hornblende, garnet, sodalite, leucite, and topaz. Clay is a hydrous aluminum silicate, $Al_2Si_2O_7,2H_2O$, formed by the decomposition of felspathic rocks. Turquois is a hydrous aluminum phosphate, $Al_2P_2O_{11},5H_2O$.

History.—Aluminum was first prepared by Woehler in 1827. The name comes from *alumen*, which term was applied from earliest times to alum and a number of other substances.

Preparation.—Aluminum is prepared by heating the chlorid with sodium or potassium, $AlCl_3 + 3Na = 3NaCl + Al$; or by electrolysis of the oxid in the presence of the fluorid.

The electrolytic method is the one now generally used. Cryolite is melted in a vessel of iron lined with carbon, and a powerful current of electricity is passed through it by means of carbon cylinders suspended in the molten rock, the vessel constituting the other electrode. Powdered aluminum oxid being added, it dissolves in the cryolite and is at once decomposed by the current. The aluminum collects in the vessel while the oxygen unites with the carbon of the cylinders. The cryolite remains unchanged, but the cylinders have to be renewed often.

Physical Properties.—Aluminum is a rather soft, bluish-white, ductile, malleable metal of specific gravity 2.58. By hammering it is hardened and its specific gravity increased to 2.68. It melts at 700°, and on cooling crystallizes in octahedrons. It can be drawn into fine wire and beaten into thin sheets, and has great tensile

strength. It is a good conductor of heat and electricity, and is very sonorous. Its market value is about 35 cents a pound.

Chemical Properties.—Aluminum is practically unchanged in the air, a thin layer of the oxid forming on the surface to protect the metal beneath. In thin sheets or in powder it burns with brilliancy to Al_2O_3. It is not attacked by water, but dissolves in solutions of various salts. It dissolves in dilute hydrochloric and sulphuric acids and in alkali hydroxids with evolution of hydrogen. In nitric acid it is scarcely soluble because of the formation of a layer of the oxid which protects the metal. It is strongly positive and is able to reduce the oxids of the more negative elements, and displaces various metals from their solutions. It combines directly when heated with chlorin, sulfur, selenium, tellurium, phosphorus, and arsenic, and forms alloys with most metals. Aluminum is trivalent, affording but the one elementary ion, $Al^{...}$.

Alloys of Aluminum.—*Aluminum Amalgam.*—The alloy of aluminum with mercury is brittle, oxidizes readily, decomposes water, and is used as a reducing agent.

Aluminum bronze, 10 per cent aluminum and 90 per cent copper, has the color of gold, takes a fine polish, and has the hardness and strength of cast iron.

Magnalium is an alloy of magnesium and aluminum.

Uses.—Because of its lightness, its toughness, its beautiful polish, and its unalterability in the air, it finds many applications in the arts. It is used in the manufacture of physical apparatus and various domestic articles. It is not well adapted for kitchen vessels and table ware, because it is attacked by dilute acids and salts. It serves for aluminum plating, especially upon copper and brass.

ALUMINUM COMPOUNDS.

Aluminum is both acidic and basic. Many of its salts are soluble in water and are electrolytes. The silicates are almost insoluble. It forms no compound with hydrogen. Some of its thermal equations are as follows:

$(Al_2O_3,H_2) = 297,000$ c. $(Al,Cl_3) = 161,000$ c. $(Al_2,S_3) = 122,400$ c.
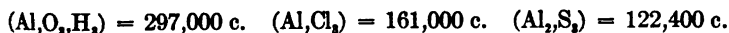
Aluminum Fluorid, AlF_3, is prepared by the action of hydrogen fluorid upon aluminum or aluminum oxid at a red heat; or by heating together calcium fluorid, aluminum oxid, and hydrochloric acid:

$$3CaF_2 + Al_2O_3 + 6HCl = 3H_2O + 3CaCl_2 + 2AlF_3.$$
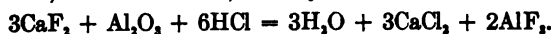
It crystallizes with 7 molecules of water in colorless rhombohedrons.

Fluoaluminic Acid, H₃AlF₆, or $\begin{array}{l} H-F = F \\ H-F = F \\ H-F = F \end{array}\Big\rangle Al$, is formed when aluminum fluorid is dissolved in hydrofluoric acid.   Its sodium salt, Na₃AlF₆, is the mineral *cryolite* found abundantly in Greenland.

Aluminum Chlorid, AlCl₃, is formed when chlorin or hydrogen chlorid is passed over heated aluminum or a heated mixture of aluminum oxid and carbon.

Aluminum chlorid forms hexagonal crystals which sublime at 183°, and melt under pressure at 193°.   At the boiling-point its density corresponds to the formula Al₂Cl₆, but above 450° dissociation takes place, and the formula is AlCl₃.   It fumes in the air and dissolves in water with the development of heat.   On evaporating the aqueous solution the crystalline hydrate, AlCl₃,6H₂O, separates. It has a strong tendency to form double salts, as AlCl₃,NaCl, and AlCl₃,3HN₃.   It is much used as a reagent in organic preparations.

Aluminum Bromid, AlBr₃, formed by direct union of the elements, is a colorless crystalline solid which melts at 80° and boils at 265°.   The hydrate, AlBr₃,6H₂O, separates from a solution of AlH₃O₃ in hydrobromic acid.

Aluminum Iodid, AlI₃, is formed by heating together aluminum and iodin.   It is a white crystalline solid, which melts at 185° and boils at 400°.   It forms the hydrate AlI₃,6H₂O.

Aluminum Oxid, Al₂O₃, is obtained by burning the metal or by igniting the hydrates or the salts of the volatile acids.   It occurs in nature as the mineral *corundum* in hexagonal prisms, and is next in hardness to diamond.   Red crystals are called *ruby,* blue ones *sapphire,* yellow ones *oriental topaz,* purple ones *oriental amethyst,* and green ones *oriental emerald.*   The emery of commerce is finely ground corundum.

The amorphous aluminum oxid artificially prepared is a soft white powder insoluble in water.   It dissolves in acids and alkalis to form salts and aluminates.

Aluminum Sulfid, Al₂S₃.   Aluminum unites to sulfur at a red heat, forming a dark-gray solid which is decomposed by water.

Aluminum forms more or less definite compounds with phosphorus, antimony boron, and carbon.

Aluminum Hydroxids.—Ammonia and alkali hydroxids precipitate $Al(HO)_3$ from solutions of aluminum salts. When this is heated to 300° it looses a molecule of water and becomes $AlO(HO)$. On further heating the rest of the water goes off and Al_2O_3 remains. Still another hydrate may be obtained by adding ammonia to a boiling solution of an aluminum salt. It is represented in the mineral *bauxite*, $Al_2O(HO)_4$.

These hydroxids are all soft, bulky, white precipitates which are both acidic and basic, dissolving in acids to form salts and in strong alkalis to form aluminates.

Aluminum hydroxid precipitates many dyestuffs from solution, uniting with them to form insoluble colored compounds called *lakes*. Upon this property depends its use as a *mordant* in dyeing and calico-printing. The cloth is immersed in an aluminum solution and then exposed to the action of steam, whereby the hydroxid is deposited upon and incorporated with the fiber. If now the cloth be dipped in the dye, the color is fixed by the aluminum hydroxid. The compounds most used for this purpose are aluminum acetate and sodium aluminate.

Aluminates.—The aluminum hydroxids are feebly acid and form a few aluminates with the strongly positive metals.

Salts of Aluminum.—Aluminum forms numerous salts with the acids, the most important of which are the sulfates and the silicates. They hydrolyze in solution and react acid.

Aluminum Sulfate, $Al_2(SO_4)_3,18H_2O$, is obtained in monoclinic tablets by dissolving the hydroxid in dilute sulfuric acid. It is used as a mordant and as a weighting material in the manufacture of paper.

The Alums.—Aluminum sulfate forms double salts with the alkali sulfates, which are all isomorphous and crystallize with 12 molecules of water in regular octahedrons or cubes. These are known as *alums*, the most important being the potassium aluminum sulfate, potash alum, or common alum of commerce, $KAl(SO_4)_2 + 12H_2O$. Its structure may be indicated thus: ·

$$K-O-SO_2-O-Al <^O_O> SO_2.$$
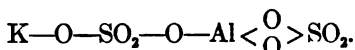
Ammonium, sodium, lithium, rubidium, cesium, thallium, and silver may take the place of potassium, and there results ammonium alum, sodium alum, etc. Again, iron chromium, manganese, indium, or gallium may replace aluminum, in which case the name in-

cludes both positive elements, as potassium chromium alum, $KCr(SO_4)_2,12H_2O$.

There is another series of double sulfates in which the alkali metal is replaced by a bivalent element, as copper iron sulfate, $CuFe_2(SO_4)_4,24H_2O$. These are called *psuedo-alums* and are not isomorphous with the other alums.

There is also a series of alums in which selenium takes the place of sulfur.

Ammonium Alum, $NH_4Al(SO_4)_2,12H_2O$, finds extensive application in the arts, being used instead of common alum on account of its cheapness.

Aluminum Nitrate, $Al(NO_3)_3,8H_2O$, deliquescent needles.

Aluminum Phosphate, $AlPO_4$, in the minerals wavelite and turquois.

Aluminum Silicates.—The original rocks of the globe and a large part of the stratified rocks (not calcareous) consist mainly of complex double silicates containing one or more of the metals, sodium, potassium, calcium, magnesium, iron, and manganese, associated most frequently with aluminum, sometimes with iron, magnesium, manganese, etc. A few characteristic compounds are as follows:

Feldspar,	$KAlSi_3O_8$.	Albite,	$NaAlSi_3O_8$.
Anorthite,	$CaAl_2Si_2O_8$.	Beryl,	$Co_3Al_2(SiO_3)_6$.
Garnet,	$Ca_3Al_2Si_3O_{12}$.	Hornblend,	$CaMgFe(SiO_3)_6$.

Clay.—In the weathering of silicious rocks the alkaline portion is converted into carbonates and dissolved away, leaving a residue of silicic oxid and aluminum silicate. The latter exists in various degrees of hydration and constitutes the substance called clay. In its purest form it is white and amorphous and is called *kaolin, porcelain clay,* or *china clay,* having usually the formula $H_2Al_2(SiO_4)_2,H_2O$. Common clay is generally red because it is mixed with iron oxid. When it is mixed with a good deal of limestone it is called *marl.*

Clay is almost infusible, but when mixed with lime or iron it melts readily. When mixed with water it forms a tough, plastic mass which may be moulded into definite forms. When moist clay is strongly heated it becomes hard and insoluble in water and acids. This burnt clay finds many applications in the arts. It is porous, but is rendered water-proof by glazing.

Bricks are made of clay containing a good deal of lime, iron, and organic matter, and when hard-burnt the surface melts, forming a natural glaze.   *Fire-bricks* are made of clay containing much silica and are hard, porous, and infusible. *Terra-cotta* is like fire-brick, but softer and burnt at a lower temperature.

Clay pipe and the coarser grades of *earthenware* are made of common clay and glazed by throwing common salt into the furnace with them.   The salt is decomposed by the hot steam into hydrogen chlorid and sodium hydroxid, and the latter unites with the clay, melting with it to a glassy surface.

Tiles are thin plates used for floors, panels, and wall-facings. They are of three kinds: *vitrified,* baked until semi-fused; *encaustic,* a facing of fine clay placèd upon a back of common clay; *glazed,* a body of uniform color, covered with a transparent glaze.

Faïence is made of white clay and covered with a white or colored glazing layer of lead silicate.   *Majolica* is a porous body covered with an opaque glaze.

Stoneware is made of rather pure clay, burned at a high temperature and glazed with salt.   *Wedgewoodware* is a fine quality of stoneware, which is made in colors, and is usually not glazed.

Porcelain is made of a mixture of feldspar, quartz, and the finest clay.   It is burnt first at a moderate temperature, then dipped in a mixture of finely ground feldspar and water, dried, and finally raised to a white heat.   It resists chemical action, stands heat well, and does not break easily.   Berlin and Meissen ware are examples.

Soft porcelain, or *chinaware,* contains less quartz and is glazed usually with lead and boric acid.   It is used for tableware and ornamental articles.

Ultramarine is a beautiful blue pigment which was formerly obtained from the rare mineral *lapis-lazuli,* but is now prepared artificially by heating together clay, sodium carbonate, charcoal, and sulfur.   By varying the process, or by treating the blue with chlorin or hydrochloric acid, green, violet, and red ultramarines are obtained.   Ultramarine blue is not affected by light, soap, or alkalis, but is destroyed by weak acids.   It is used for laundry blue, for pigments, for printers' ink, and in printing wallpaper and calico.   Its chemical formula has not been ascertained, but it seems to be a mixture of sodium aluminum silicate with sodium polysulfids.

GALLIUM.

Symbol Ga. Atomic weight 70. Valence III. Specific gravity 5.9. Melting-point 30°.

Occurrence.—Gallium is one of the rarest of all elements. Its chief source is certain zinc blendes, which are considered rich in gallium if they contain 0.002 per cent. Boisbaudran and Jungfleisch obtained 62 grams from 2400 kilograms of blende.

History.—In 1875, Lecoq de Boisbaudran discovered gallium by means of the spectroscope in a zinc blende from the Pyrenees Mountains, and named it after ancient Gaul. It is found to be identical with the eka-aluminum whose existence was predicted by Mendeleeff. Its spectrum contains two characteristic violet lines.

Preparation.—Gallium is obtained by electrolysis of an ammoniacal solution of the sulfate.

Properties.—Gallium is a silver-white crystalline metal, rather hard, scarcely malleable, and ductile, and with specific gravity 5.9. It has the remarkably low melting-point of 30°. The melted metal remains liquid indefinitely at the ordinary temperature, or even at 0°, but solidifies at once on coming in contact with a fragment of the solid metal. It is only superficially oxidized in the air, dissolves in hydrochloric acid, and alkalis with evolution of hydrogen, and in nitric acid evolving oxids of nitrogen. It is very costly, the market price being about $180 a gram, or $80,000 a pound.

COMPOUNDS OF GALLIUM.

Gallium is trivalent, but in a few compounds seems to be a dyad. Because of its rarity and costliness its compounds have not been well studied. Only a few need be mentioned here.

Gallium Chlorid, $GaCl_3$, melts at 75° and boils at 215°.

Gallium Dichlorid, $GaCl_2$, or Ga_2Cl_4, melts at 164° and boils at 535°.

Bromids and iodids corresponding to the chlorids have been prepared.

Gallium Monoxid, GaO, is obtained by reducing Ga_2O_3 in a stream of hydrogen. It is basic and unstable.

Gallium Oxid, Ga_2O_3, is obtained by heating gallium nitrate. It is mainly basic, but with the strongest alkalis is acidic.

Gallium Hydroxid, GaH_3O_3, is precipitated by ammonia from solutions of gallium salts.

Gallium Salts.—Gallium hydroxid dissolves in acids to form salts. The most important are the nitrate, $Ga(NO_3)_3$, and the sulfate, $Ga_2(SO_4)_3$. The sulfate forms alums such as *ammonium gallium alum,* $(NH_4)Ga(SO_4)_2,12H_2O$.

INDIUM.

Symbol In.   Atomic weight 114.   Valence I and III.   Specific gravity 7.4.   Melting-point 176°.

History and Occurrence. — Indium was discovered by Reich and Richter in 1863 through a bright indigo-blue line in its spectrum, whence its name.   It occurs in very minute quantities in zinc blendes from Freiberg and the Hartz Mountains and in the solar atmosphere (Lockyer).

Preparation.—Indium is prepared by reducing the oxid in a current of hydrogen, or by treating its salts with zinc.

Properties.—Indium is a white, malleable, amorphous metal, softer than lead, and of specific gravity 7.4.   It melts at 176° and distils at white heat.   It tarnishes in the air and burns with a blue flame to In_2O_3. It dissolves readily in nitric acid, but with difficulty in hydrochloric and sulfuric acids.

COMPOUNDS OF INDIUM.

The valence of indium is I and III, and in a few cases apparently II.

Indium Chlorid, $InCl_3$, is formed when indium is treated with an excess of chlorin.   It is a white, shining crystalline solid which sublimes at 440°.   InCl and $InCl_2$ have been prepared.

Chlorindic Acid, H_3InCl_6, is formed by action of hydrochloric acid upon indium chlorid.   It forms well-defined salts.

Indium Bromid, $InBr_3$, and **Indium Iodid,** InI_3, are crystalline solids, the former white and the latter yellow.

Indium Oxid, In_2O_3, is a yellow powder obtained by burning indium in the air.   It dissolves slowly in cold, easily in warm, acids.

Indium Hydroxid, InH_3O_3, is precipitated by alkalis from indium solutions.   The oxid and hydroxid are decidedly basic, but at the same time weakly acidic.

Indium Sulfid, In_2S_3, is a yellow solid formed by direct union of the elements, or by action of hydrogen sulfid upon indium solutions.

Indium Salts.—The oxid and hydroxid of indium dissolve in the acids to form salts.   The principal ones are the carbonate, nitrate, sulfite, and sulfate.   It forms alums; as *potassium indium alum,* $KIn(SO_4)_2,12H_2O$.

TERBIUM.

Symbol Tb.   Atomic weight 160.   Valence III.

Occurrence.—Terbium is one of the rare elements and has not been well investigated.   It occurs in the gadolinite earths, but more abundantly in the mineral samarskite of North Carolina, which is a columbate of iron, yttrium, erbium, and terbium.   The name is a contraction of Ytterby, a town in Sweden.

But a few compounds have been studied. *Terbium oxid*, Tb_4O_3, is an órange-yellow powder, and *terbium sulfate*, $Tb_2(SO_4)_3,8H_2O$, forms colorless crystals.

THALLIUM.

Symbol Tl. Atomic weight 204. Valence I and III. Specific gravity 11.8. Melting-point 290°.

Occurrence.—Thallium occurs widely distributed in small quantities. The mineral *crooksite*, from Sweden, contains 17 per cent of Tl_2Se_3, along with selenids of copper and silver. It is found in copper and iron pyrites and in many other minerals, in the water of certain springs, and in commercial hydrochloric and sulfuric acids.

History.—Thallium was discovered by Crookes, in 1861, by means of the spectroscope, in the leaden chamber deposit of the sulfuric acid manufacture. He called it *thallium*, from the bright-green line seen in its spectrum. It was also discovered independently by Lamy in the same way and about the same time.

Preparation.—Is best prepared by electrolysis of the sulfate.

Properties.—Thallium is a white crystalline metal, malleable, ductile, soft as sodium, and of specific gravity 11.8. It melts at 290° and distils at white heat. It tarnishes in the air, but may be kept under water which is free from air. It makes a green mark upon paper, which soon disappears by oxidation. It burns with a beautiful green flame to Tl_2O. It dissolves in acids, except hydrochloric, in which it becomes covered with the insoluble chlorid. It is displaced from its compounds by zinc and cadmium.

THALLIUM COMPOUNDS.

The valence of thallium is I and III. In its thallous compounds it resembles the alkali metals; in the others it is much like aluminum, but presents many differences. In its physical properties it resembles lead; in its halids, silver and mercury. The thallous ion is colorless and univalent, the thallic ion is slightly yellow and passes easily to the thallous ion.

Thallous Fluorid, TlF, soluble salt obtained by dissolving the carbonate in hydrofluoric acid.

Thallous Chlorid, TlCl, a white solid formed by the action of hydrochloric acid upon thallous solutions, melts at 427° and boils at 715°. It forms double salts, as $PtCl_4,2TlCl$.

Thallic Chlorid, $TlCl_3$, formed by direct union, or by the action of HCl upon thallium or thallous chlorid; colorless deliquescent crystals.

Thallous Bromid, TlBr, yellow precipitate.

Thallous Iodid, TlI, yellow crystalline solid, melts at 190°.

Thallous Oxid, Tl$_2$O, obtained by heating the hydroxid to 100°, is a black powder which melts at 300°. It dissolves in water to form thallous hydroxid.

Thallous Hydroxid, TlHO, long soluble needles.

Thallic Oxid, Tl$_2$O$_3$, obtained by burning thallium, is a dark-red powder, insoluble in water and alkalis.

Thallic Hydroxid, TlH$_3$O$_3$, is precipitated by bases from solutions of thallic salts as a brown precipitate. When dried it loses water and becomes the metahydroxid TlO(HO).

Thallous Sulfid, Tl$_2$S, is precipitated as a black powder by hydrogen sulfid from neutral solutions of thallous salts.

Thallic Sulfid, Tl$_2$S$_3$, is a black solid formed by direct union.

Salts of Thallium.—The thallous salts are more easily formed and more stable than the thallic salts. Some of the more important compounds are thallous chlorate, TlClO$_3$; perchlorate, TlClO$_4$; sulphate, Tl$_2$SO$_4$; nitrate, TlNO$_3$; orthophosphate, Tl$_3$PO$_4$; acid phosphates, HTl$_2$PO$_4$ and H$_2$TlPO$_4$; carbonate, Tl$_2$CO$_3$; acid carbonate, HTlCO$_3$; silicate, Tl$_6$Si$_{10}$O$_{23}$; thallic sulfate, Tl$_2$(SO$_4$)$_3$,7H$_2$O; nitrate, Tl(NO$_3$)$_3$,8H$_2$O; thallium alum, TlAl(SO$_4$)$_2$,12H$_2$O.

CHAPTER XXXIII.

GROUP III A. THE SCANDOIDS. SCANDIUM GROUP.

Scandium 44. Yttrium 89. Lanthanum 139. Ytterbium 173.

The elements of this group are very rare and are found only in certain localities and in a few rare minerals. They are trivalent, and their oxids, hydroxids, and salts are similar to those of the elements of the boron group. They do not form alums, and their oxalates are insoluble. They are all basic, showing but the slightest acid character.

SCANDIUM.

Symbol Sc. Atomic weight 44. Valence III.

History and Occurrence.—Scandium has not been isolated. The oxid was discovered by Nilson, in 1879, in the minerals euxenite and gadolinite, from Sweden. It was also found by Cleve in the same minerals. Nilson named it after Scandinavia. Scandium takes the place of the eka-boron described by Mendeleef. Its salts give brilliant spectra.

Scandium Chlorid, $ScCl_3$, crystalline solid, gives characteristic spectrum.

Scandium Oxid, Sc_2O_3, is a white infusible powder of specific gravity 3.86, obtained by igniting the hydroxid, nitrate, or oxalate.

Scandium Hydroxid, ScH_3O_3, is precipitated by alkalis from solutions of scandium salts.

Scandium Nitrate, $Sc(NO_3)_3$, prismatic crystals.

Scandium forms double sulfates like $K_3Sc(SO_4)_3$, which are not alums and are insoluble in potassium sulfate solution.

YTTRIUM.

Symbol Y. Atomic weight 89. Valence III.

History and Occurrence.—In 1794 Gadolin found a new earth in Gadolinite and in 1797 Ekeberg named it *yttria* from Ytterby in Sweden.

Preparation.—Yttrium is prepared by heating the chlorid with potassium, or by electrolysis of potassium yttrium chlorid.

Properties.—Yttrium is a gray powder which is soluble in acids, decomposes water, and burns brilliantly to Y_2O_3.

Yttrium Chlorid, YCl_3, gives a characteristic spectrum and forms double compounds with alkali chlorids.

Yttrium Oxid, Y_2O_3, is obtained by heating the hydroxid.

Yttrium Hydroxid, YH_3O_3, is precipitated by alkalis from yttrium solutions.

Yttrium Nitrate, $Y(NO_3)_3$, is more stable than the other nitrates of the group.

Potassium Yttrium Sulfate, $K_2Y_2(SO_4)_6$, is soluble in potassium sulfate solution and serves to separate yttrium from cerium, lanthanum, and scandium.

Yttrium Carbonate, $Y_2(CO_3)_3$, is formed when the hydroxid is exposed to the air.

LANTHANUM.

Symbol La.   Atomic weight 138.9.   Valence III.

Occurrence.—Lanthanum is a constituent of cerite, gadolinite, orthite, and other rare minerals. *Lanthanite* from Bethlehem, Pa., is a carbonate of lanthanum and other metals.

History.—The ceria discovered by Klaproth, in 1803; was shown by Mosander, in 1839, to contain two oxids. He retained the name ceria for one and called the other *lanthana* (concealed). In 1841 he discovered that lanthana was mixed with another oxid which he called *didymia*.

Preparation.—Lanthanum is best prepared by electrolysis of the chlorid.

Properties.—Lanthanum is a white metal, malleable, ductile, and of specific gravity 6.16. It tarnishes and burns in the air, decomposes water, and dissolves in acids. It combines directly with chlorin, bromin, and iodin. Lanthanum is trivalent and forms numerous compounds, most of which have been but little studied.

Lanthanum Chlorid, $LaCl_3$, is obtained as white crystals by adding ammonium chlorid to hydrochloric acid solution of lanthanum oxid. It forms double salts with other chlorids, and yields a characteristic spectrum.

Lanthanum forms also *oxychlorid, fluorid, oxyfluorid, bromid, oxybromid, iodid,* and *cyanid.*

Lanthanum Oxid, La_2O_3, is obtained as a white amorphous powder by heating the hydroxid or oxalate. It dissolves in acids and unites with water. It is infusible, and when strongly heated emits a dazzling white light. An arrangement for obtaining light by heating it and other related oxids in the Bunsen flame was patented by von Welsbach, and is much used as a gas attachment under the name of the *Welsbach burner.*

Lanthanum Hydroxid, LaH_3O_3, is precipitated by alkali hydroxids from lanthanum solutions. It is strongly basic and dissolves in the acids to form salts.

Lanthanum Sulfid, La$_2$S$_3$, yellow crystalline solid.

Lanthanum Salts.—Lanthanum forms numerous salts which cannot here be described in detail. They are mostly colorless, crystallize well, and those which are soluble have an astringent taste. The sulfate forms double salts with the alkali sulfates which are not alums. There are also a few basic salts. The following are the most important: chlorate, perchlorate, chlorite, hypochlorite, bromate, iodate, periodate, sulfate, sulfite, thiosulfate, selenate, selenite, molybdate, tungstate, nitrate, phosphate, phosphite, arsenate, arsenite, and silicate.

YTTERBIUM.

Symbol Yb.   Atomic weight 173.   Valence III.

History and Occurrence.—Ytterbium has not been isolated. It occurs along with the other metals of the group in gadolinite and euxenite. It was discovered gradually through the investigations of several men. especially Marignac and L. F. Nilson. It was named by Marignac for Ytterby, a town in Sweden.

Compounds of Ytterbium.—Ytterbium is trivalent and forms compounds analogous to those of lanthanum.

Ytterbium Oxid, Yb$_2$O$_3$, is a white infusible powder which gives a fine emission spectrum. **Ytterbium hydroxid,** YbH$_3$O$_3$, is precipated by ammonia from ytterbium solutions.

Ytterbium Salts.—Ytterbium forms the usual salts of the group. The oxalate is insoluble in water and serves to remove it from its solutions.

CHAPTER XXXIV.

GROUP II A. THE GLUCINOIDS. MAGNESIUM GROUP. ALKALI-EARTH METALS.

Glucinum **9.1.** Magnesium **24.36.** Calcium **40.** Strontium **87.6.** Barium **137.4.**

The term *earth* was applied by the older chemists to all substances which were insoluble and infusible and not metallic in appearance. It afterwards came to represent the oxids, which were supposed to be elements until Davy in 1808 showed that they were compounds of oxygen and metals. It was observed that they were mostly alkaline in reaction and neutralized acids. They were therefore called *alkali earths*.

The elements of this sub-group have the valence II, calcium only acting in a few cases as a tetrad. They form similar oxids, hydroxids, and salts, and the chemical activity and stability of the compounds increase with the atomic weight. With the exception of glucinum, they decompose water, barium acting with great vigor. The carbonates and hydroxids are decomposed by heat with increasing difficulty, those of barium being fusible without decomposition. All are strongly basic, but glucinum dissolves in strong alkalis to form unstable salts.

Calcium, strontium, and barium are nearly related and are frequently taken together and called the calcium group. They have characteristic spectra and color flames, calcium purple-red, strontium crimson, and barium green. Glucinium and magnesium resemble them in their general characters, but are also much like zinc, cadmium, and mercury forming, for example, soluble sulfates and double salts. The following table illustrates the group analogies:

	Atomic Weight.	Specific Gravity.	Specific Heat.	Oxids.	Peroxids.	Chlorids.	Sulfates.
Glucinum.......	9	1.64	0.62	GlO	....	$GlCl_2$,	$GlSO_4$
Magnesium......	24	1.74	0.25	MgO	....	$MgCl_2$	$MgSO_4$
Calcium	40	1.57	0.17	CaO	CaO_2	$CaCl_2$	$CaSO_4$
Strontium.......	87	2.50	0.078?	SrO	SrO_2	$SrCl_2$	$SrSO_4$
Barium..........	137	3.75	0.047?	BaO	BaO_2	$BaCl_2$	$BaSO_4$

GLUCINUM (BERYLLIUM).

Symbol Gl.   Atomic weight 9.1. Valence II.   Melting-point 1000°.

Occurrence.—The principal native compound of glucinum is *beryl,* a glucinum aluminum silicate, $Gl_3Al_2(SiO_3)_6$. The transparent green crystals are called *emerald* and the bluish-green ones *aquamarine.* Other compounds are *phenacite,* Gl_2SiO_4, and *chrysoberyl,* $GlAl_2O_4$.

History.—In 1797, Vauquelin showed that beryl contained a peculiar earth, and in 1827 the metal was isolated by Wöhler, but pure glucinum was first prepared by Humpidge in 1885.   The name refers to the fact that its soluble compounds have a sweet taste. The name beryllium, which is commonly used in Europe, comes from the mineral beryl.

Preparation.—Glucinum is prepared by heating the chlorid with sodium in an atmosphere of hydrogen, or by heating the oxid with magnesium, or by electrolysis of its compounds.

Properties.—Glucinum is a white, ductile, malleable metal of specific gravity 1.64.   Its specific heat at the ordinary temperature is only 0.4, or about half what it should be according to the law of Dulong and Petit, but at 500° it is 0.62, and no doubt at a higher temperature it would follow the law.   It does not tarnish in the air, but when heated becomes covered with the oxid, and when finely divided burns with a white light. It decomposes hot water slowly and dissolves in acids.   It is usually basic, but with strong alkalies forms *glucinates,* as K_2GlO_2.   The ion $Gl^{..}$ is colorless and has a sweetish taste.

GLUCINUM COMPOUNDS.

Glucinum Chlorid, $GlCl_2$, is obtained by heating the oxid with charcoal in a stream of chlorin.   It is a white deliquescent solid which crystallizes with four molecules of water.

Glucinum Oxid, GlO, is obtained by heating the hydroxid.   It is a white amorphous powder, insoluble in water, soluble in acids and strong alkalis.   When very strongly heated it becomes crystalline.

Glucinum Hydroxid, GlH_2O_2, is thrown down by ammonia from glucinum solutions as a gelatinous precipitate, soluble in acids and strong alkalis.   The alkali solution contains the alkali glucinate, (K_2GlO_2), which is unstable, precipitating GlH_2O_2 on standing.   With ammonium carbonate it is changed into basic glucinum carbonate.

Glucinum Sulfate, $GlSO_4$, is prepared by dissolving glucinum hydroxid in dilute sulfuric acid, and crystallizes from the solution with four molecules of water.   When the solution is heated with glucinum hydroxid, basic salts are formed such as Gl_2SO_4 or $O\diagdown\!\!\begin{matrix} Gl{-}O \\ Gl{-}O \end{matrix}\!\!\diagup S\diagup\!\!\begin{matrix} O \\ O \end{matrix}$

Glucinum Nitrate, $Gl(NO_3)_2,3H_2O$, is a deliquescent solid, soluble in water and alcohol.   When gently heated it forms the basic nitrate $Be(HO)NO_3,H_2O$.

Glucinum Phosphates.—Various phosphates may be formed, as $GlHPO_4,3H_2O$, $GlH_4(PO_4)_2$, and $(NH_4)_2Na_2Gl(PO_4)_2,7H_2O$.

Glucinum Carbonate, $GlCO_3,4H_2O$, is obtained by passing carbon‧ dioxid through water containing the basic carbonate in suspension. By action of alkali carbonates upon glucinum solutions *basic carbonates* are obtained, as $Gl_2CO_5,5H_2O$, or $Gl < ^{O—Gl—O}_{O—Gl—O} > CO$.

<div align="center">MAGNESIUM.</div>

Symbol Mg. Atomic weight 24.36. Valence II. Specific gravity 1.74. Melting-point 750°.

Occurrence.—The compounds of magnesium are abundant and widely distributed. *Magnesite*, $MgCO_3$, occurs in considerable quantity, and *dolomite*, a double carbonate of magnesium and calcium, $(MgCa)CO_3$, is a common rock found in mountain masses. Magnesium sulfate occurs as the mineral *kieserite*, $MgSO_4,H_2O$, and in solution in many terrestrial waters. Magnesium is found in plants and animals, being a small constituent of bones, blood, shells, and cereal grains, and in many native silicates.

History.—Magnesium sulfate was first obtained by a London physician, Nehemiah Grew, in 1695, by evaporating the water of the mineral spring at Epsom. It was afterward much used as a medicine under the name of *Epsom salt*. About the same time magnesium carbonate was introduced as a medicine under the name of *magnesia alba*. The oxid and metal were obtained by Davy in 1800, and the metal purer by Bussy in 1830. Bunsen obtained the metal by electrolysis.

The name magnesia was applied to the native manganese dioxid or pyrolusite, because of its supposed magnetic properties. The two metals gradually acquired their present names.

Preparation.—Magnesium may be prepared by electrolysis of the chlorid, or by heating with sodium the chlorid or the double chlorid, $MgCl_2,KCl$.

Physical Properties.—Magnesium is a silver-white, malleable, ductile metal of specific gravity 1.74 and specific heat 0.245. It melts at about 750° and distils at a red heat. It is moderately hard, has small tenacity, and crystallizes in hexagonal prisms isomorphous with zinc.

Chemical Properties.—Magnesium tarnishes in moist air and when heated burns with a brilliant white light very rich in actinic

rays. It does not decompose water, but oxidizes in superheated steam. It dissolves readily in acids, but not in alkalis, and is therefore wholly basic. It unites directly with chlorin and nitrogen. It is a powerful reducing agent, being able to separate silicon and boron from their oxids. It forms with many metals alloys which are brittle and of no commercial importance.

Uses.—Magnesium is mainly used as a source of light and as a reducing agent. The light is applied in signalling in the army and navy, in pyrotechny, and in photography. Flash-light powder is magnesium or a mixture of magnesium and zinc.

<div align="center">MAGNESIUM COMPOUNDS.</div>

Magnesium is strictly bivalent and chemically quite active. It unites with most of the negative elements and forms salts with nearly all the acids. Its salts may be normal, acid, basic, or double, and are generally soluble in water. They are obtained by dissolving the metal, the oxid, or the hydroxid in acids. The magnesium ion is colorless and bivalent, Mg''.

The heat of formation of some magnesium compounds is as follows:

$(Mg,O) = 143,900$ c. $(Mg,H_2,O_2) = 217,300$ c. $(Mg,S) = 77,600$ c.
$(Mg,Cl_2) = 151,000$ c. $(Mg,S,O_4) = 302,300$ c. $(Mg,N,O_6,6Aq.) = 210,500$ c.

Magnesium Fluorid, MgF_2, occurs in the mineral *sellaite*.

Magnesium Chlorid, $MgCl_2$, occurs in sea-water and salt springs, and crystallizes from solution with 6 molecules of water. It has a bitter taste and is used in dressing cotton goods.

Potassium Magnesium Chlorid, $KMgCl_3,H_2O,(K — Cl = Cl — Mg — Cl)$, occurs as the mineral *carnallite*.

Ammonium Magnesium Chlorid, $NH_4MgCl_3,6H_2O$, forms rhombic crystals.

Calcium Magnesium Chlorid, $CaCl_2,2MgCl_2,12H_2O$, occurs as the mineral *tachhydrite*.

Magnesium Bromid, $MgBr_2,6H_2O$, is found in sea-water and salt springs.

Magnesium Iodid, MgI_2, is found in sea-water.

Magnesium Oxid, MgO, is obtained by burning magnesium or by igniting the hydroxid, carbonate, or nitrate. It is a loose, white, tasteless, powder, slightly soluble in water, easily soluble in acids. It is known as *magnesia* or *calcined magnesia*, and is used in medicine as an antacid and as a soothing application. It stands a high tem-

perature without melting, and is therefore used for crucibles and for lining stoves and furnaces. It melts in the oxyhydrogen flame and cools to a compact solid hard as glass.

Magnesium Hydroxid, MgH_2O_2, occurs in nature as the mineral *brucite,* crystallized in rhombohedrons. It is precipitated from magnesium solutions by alkali hydroxids. It is a light, white powder, insoluble in water and alkalis, soluble in acids and ammonium salts. It is converted by the carbon dioxide of the air into the carbonate. It is strongly basic, and while the compound K_2MgO_2 does not exist, the analogous salt, K_2MgCl_4 or $\begin{smallmatrix} K-Cl=Cl \\ K-Cl=Cl \end{smallmatrix} \Big\rangle Mg$, has been prepared.

Magnesium Sulfid, MgS, is a yellow powder formed by direct union.

Magnesium Hydrosulfid, MgH_2S_2, and **Magnesium Selenid,** MgSe, have been prepared.

Magnesium Nitrid, Mg_3N_2, is a yellow-green amorphous mass obtained by igniting magnesium in nitrogen.

Magnesium Phosphid, Mg_3P_2, is a hard gray solid obtained by heating magnesium with phosphorus in an atmosphere of hydrogen.

Magnesium Arsenid, Mg_3As_2, is a brown mass obtained by direct union.

Magnesium Silicid, Mg_2Si, is prepared by heating together magnesium chlorid, sodium fluosilicate, sodium chlorid, and sodium. It is decomposed by hydrochloric acid, yielding hydrogen silicid, H_4Si.

Magnesium Borid, Mg_3B_2, is obtained by fusing together boron trioxid and magnesium.

Magnesium Sulfate, $MgSO_4$, occurs with various degrees of hydration. The mineral kieserite is $MgSO_4,H_2O$, scarcely soluble in water. As obtained by evaporating its solution at the ordinary temperature it forms rhombic prisms or needles of composition $MgSO_4,7H_2O$. Crystallized above 70° it has only $6H_2O$, while at 0° it holds $12H_2O$. When heated it easily loses all but one molecule of water, and this is expelled only above 200°. The salt is therefore probably a derivative of the monometa sulfuric acid, H_4SO_5, and should be written for the common form $MgH_2SO_5,6H_2O$. It has a bitter, salty, sickening taste and acts as a cathartic. It is found in most terrestrial waters and is abundant in the water of many mineral springs and wells. It is used as a medicine, as a fertilizer, in the manufacture of other sulfates, and for loading cotton goods.

Magnesium sulfate forms double salts with other sulfates, crystallizing in monoclinic prisms with six molecules of water, as

$K_2SO_4,MgSO_4,6H_2O$, or $K_2Mg(SO_4)_2,6H_2O$. These are isomorphous with similar salts of zinc, iron, cobalt, and nickel. The structure is probably this: $\begin{matrix} K-O-SO_2-O \\ K-O-SO_2-O \end{matrix}\Big\rangle Mg$.

Other salts which can only be mentioned in this connection are bromate, hypochlorite, chlorate, perchlorate, iodate, periodate, thiosulfate, sulfite, selenate, selenite, tellurate, tellurite, chromate, molybdates, tungstates, and uranates, vanadates, columbates, tantalates, and borates.

Magnesium Nitrate, $Mg(NO_3)_2,6H_2O$, is a crystalline solid obtained by dissolving magnesium oxid in nitric acid.

Magnesium Phosphate, $Mg_3(PO_4)_2$, occurs in bones and in cereal grains.

Magnesium Hydrogen Phosphate, $MgHPO_4$, is precipitated from solutions of magnesium sulfate by sodium phosphate.

Magnesium Ammonium Phosphate, $MgNH_4PO_4,6H_2O$, is precipitated from magnesium solutions by disodium hydrogen phosphate in the presence of ammonia and ammonium chlorid. It is a fine crystalline powder which loses $5H_2O$ at 100°, and at a red heat becomes magnesium pyrophosphate, $Mg_2P_2O_7$.

Magnesium Arsenate, $Mg_3(AsO_4)_2$, and **magnesium ammonium arsenate,** $MgNH_4AsO_4$, are very similar to the corresponding phosphates.

Magnesium Carbonate, $MgCO_3$, occurs as *magnesite,* isomorphous with calcium carbonate. It is precipitated by sodium carbonate from solution of magnesium chlorid. It has specific gravity 3, and dissolves in water containing carbon dioxid. It crystallizes with 3 or 5 molecules of water, according to the temperature. It forms double carbonates, of which the best example is dolomite.

Basic Magnesium Carbonate.—If a magnesium salt be boiled with sodium or potassium carbonate, a crystalline basic carbonate is thrown down. This is the *magnesia alba* of commerce and consists mainly of the compound $Mg_3H_2C_2O_8$, or $2MgCO_3,MgH_2O_2$, or $H-O-Mg-O-CO-O-Mg-O-CO-O-Mg-O-H$. It is almost insoluble in water, but dissolves in ammonium salts, hence ammonium carbonate does not precipitate a magnesium salt in the presence of ammonium chlorid.

Magnesium Silicates.—Magnesium enters into the composition of many silicates. Olivine is the simple magnesium orthosilicate, Mg_2SiO_4; enstatite is the metasilicate, $MgSiO_3$; serpentine is a magnesium disilicate, $Mg_3Si_2O_7,2H_2O$; talc is magnesium hydrogen silicate, $Mg_3H_2Si_4O_{12}$, as is also meerschaum, $Mg_2H_2Si_3O_9,H_2O$; asbestus is calcium magnesium silicate, $CaMg(SiO_3)_2$; and so on.

CALCIUM.

Symbol Ca. Atomic weight 40. Valence II and IV. Specific gravity 1.57. Melting-point 800°

Occurrence.—The most important native compound of calcium is the carbonate, $CaCO_3$, which occurs as *calcite* in rhombohedrons, and as *aragonite* in rhombic prisms, and in large masses in the rocks *limestone, marble, chalk, oolite,* and *travertine.* *Dolomite* is a magnesian limestone, $(CaMg)CO_3$. The sulfate occurs as *gypsum, selenite,* and *alabaster,* $CaSO_4,H_2O$, and as *anhydrite,* $CaSO_4$. *Fluorite* or *fluor spar* is CaF_2, *apatite* is $Ca_3(PO_4)_2$, with varying quantities of $CaCl_2$ and CaF_2. Calcium is a constituent of many silicates; *wallastonite* is simple calcium silicate, $CaSiO_3$, and *pyroxene* is a calcium magnesium silicate.

The carbonate and sulfate of calcium are found in almost all terrestrial waters; the phosphate in bones; the carbonate in shells, egg-shells, and coral; and various salts in the bodies of plants and animals. The element is found in the sun, meteorites, and fixed stars.

History.—The use of lime for mortar and the method of making it by burning limestone were known to the ancients. The name is from the Latin *calx,* lime. In 1722 Fr. Hofmann showed that lime was a distinct earth, and the metal was obtained by Davy in 1808 by electrolysis of the oxid.

Preparation.—Calcium is one of the most abundant of the elements, but it is separated from its compounds with so much difficulty that it is really a rare and costly object. It may be prepared by electrolysis of the fused chlorid; or by heating the iodid with sodium; or by heating the chlorid with sodium and zinc, whereby an alloy of zinc and calcium is obtained from which the zinc is driven off by heat.

Physical Properties.—Pure calcium prepared from the iodid is a white, lustrous, crystalline solid, hard as limestone, ductile and malleable, and of specific gravity 1.58. It melts at 800°. away from the air. As ordinarily prepared it has a brass-yellow color.

Chemical Properties.—Calcium is not readily attacked by oxygen, chlorin, bromin, or iodin, but unites with them when heated. It tarnishes in moist air and is gradually converted into the hydroxid and carbonate. It decomposes water, but with less energy than sodium and potassium; it burns when heated in the air, uniting

with both oxygen and nitrogen; it dissolves readily in the acids; it forms alloys with aluminum, antimony, lead, mercury, sodium, and zinc. It has not been prepared in quantity, and is of no use in the arts.

CALCIUM COMPOUNDS.

Calcium is bivalent, but in a few cases exhibits the valence IV. It is chemically quite active and forms an immense number of compounds. Like magnesium it has a tendency to form double salts with the allied elements. Its compounds, with the exception of the carbonate, phosphate, and silicates, are generally soluble in water. Its free ion in solutions is Ca''.

Some of the thermal equations are as follows:

(Ca,O) = 131,000 c. (Ca,H_2,O_2) = 214,900 c. (Ca,S) = 89,600 c.
(Ca,Cl_2) = 169,800 c. (Ca,Br_2) = 140,900 c. (Ca,I_2) = 107,300 c.
(Ca,S,O_4) = 318,400 c. (Ca,N_2,O_6) = 202,600 c. (Ca,C,O_3) = 270,400 c.
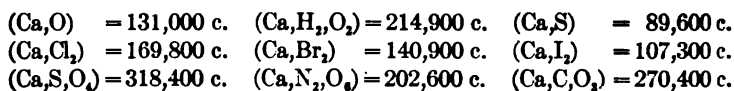
Calcium Fluorid, CaF_2, occurs in nature as fluorite or fluor-spar in cubes and octahedrons, white or colored by impurities. It is found in plants, in bones, and in teeth, in sea-water, and in the waters of certain mineral springs. It is nearly insoluble in water, but dissolves in strong acids. Heated with sulufric acid it yields hydrogen fluorid, a substance much used in etching glass. It is the principal source of fluorin compounds, and is used as a flux in the smelting of certain ores, whence its name, *fluo, I flow.*

Fluor-spar after having been heated is luminous in the dark, a phenomenon which is called *fluorescence*, and which was first mentioned by Elsholz in 1677, and again noted by Leibnitz in 1710.

Calcium Chlorid, $CaCl_2$, is found in nature combined with other chlorids, as in the mineral tachhydrite, $CaCl_2,2MgCl_2,12H_2O$, and also in sea-water. It is prepared by dissolving salts of calcium in hydrochloric acid and is a waste product in the manufacture of ammonia and soda. It has a strong attraction for water and is very deliquescent. It crystallizes with $6H_2O$ in hexagonal prisms, which loose four molecules of water at 200°, and the whole of it at a higher temperature. It melts at red heat and cools to a crystalline mass of specific gravity 2.2. It dissolves in its own weight of water at the ordinary temperature, and more as the temperature rises. A solution containing two parts of the salt to one of water boils at

158°. Such solutions are used for baths where high temperatures are desired. It forms a freezing mixture with ice, in which the thermometer reads as low as $-48°$. It is used as a drying agent for gases except ammonia, with which it forms a compound, $CaCl_2,8NH_3$.

Calcium Bromid, $CaBr_2$, is obtained by dissolving calcium salts in hydrobromic acid as white, lustrous, deliquescent needles.

Calcium Iodid, CaI_2, is obtained by dissolving calcium hydroxid in hydriodic acid, or by the action of iodin on calcium sulfid suspended in water. It is a white deliquescent solid, soluble in water, alcohol, and ammonia.

Calcium Oxid, CaO, is obtained by igniting the carbonate or nitrate

$$CaCO_3 = CO_2 + CaO, \qquad Ca(NO_3)_2 = N_2O_5 + CaO.$$

It is known as *lime* or *quicklime* and is prepared in quantities by burning limestone or marble in kilns.

Calcium oxid is a white amorphous solid of specific gravity 2.3 to 3.0. It unites with water with great vigor, evolving much heat and becoming the hydroxid, CaH_2O_2, which is known as *slaked lime*. On exposure to air it absorbs moisture and carbon dioxid and becomes a mixture of the oxid, hydroxid, and carbonate, which is called *air-slaked lime*. If the rock from which the lime is made is pure it is said to be *fat* or *rich lime;* if the rock contains much magnesium or clay, the lime is said to be *poor*, and slakes slowly.

Lime is of great commercial importance and has many applications in the arts. On account of its affinity for water it is a powerful drying agent both for gases and liquids. It is useful as a disinfectant and a fertilizer. It is practically infusible, melting at about 3000°, and when heated in the oxy-hydrogen flame it emits a very brilliant white light, known as the *lime-light*, and used for projections. It is employed in the manufacture of ammonia, caustic alkalis, bleaching powder, and potassium chlorate, and in tanning to remove the hair from the hides. It is largely used in mortars and cements. *Soda-lime* is obtained by slaking lime with sodium hydroxid solution.

Calcium Hydroxid, CaH_2O_2, is formed by the union of calcium oxid and water, $CaO + H_2O = CaH_2O_2$. At a red heat the reaction is reversed, $CaH_2O_2 = CaO + H_2O$. It is also obtained as a white precipitate by the action of caustic alkalis upon calcium chlorid, $2KHO + CaCl_2 = CaH_2O_2 + 2KCl$. If the calcium chlorid solution is concentrated, the whole mass becomes solid.

Calcium hydroxid is a fine white powder of specific gravity 2. It dissolves sparingly, 100 parts of cold water taking 0.14 part, while boiling water dissolves only half so much. The clear solution is known as *lime-water*. If water be shaken with more lime than it will dissolve a thin emulsion is obtained which is called *milk of lime*.

Calcium hydroxid is alkaline and strongly basic, forming salts with nearly all the acids. It unites with the carbon dioxid of the air to form the carbonate. This causes the crust on the surface of lime-water and the precipitate when carbon dioxid is passed through it.

Mortars and Cements.—Mortar consists of one part of lime and three or four parts of sharp quartz sand made into a paste with water. When placed in the wall it "sets" in a few days, because of the loss of water, and gradually hardens because of the formation of calcium carbonate by means of carbon dioxid absorbed from the air.

If the rock contains 10 or more per cent of silica, the lime made from it yields a mortar which hardens rapidly and even under water. This is called *hydraulic lime* or *cement*. Such cement may be obtained by mixing lime and clay in due proportion and then igniting. If the clay amounts to 30 or 35 per cent, the mortar hardens in two or three hours. The original *Roman cement* was made from a mixture of lime with a volcanic tufa found near Naples. *Portland cement* is essentially a mixture of chalk and clay with some iron and magnesium. The materials are carefully mixed in exact proportions and ground together with water, then dried and burned. This is the strongest of all cements.

Bleaching-powder or **Chlorid of Lime** is prepared on a large scale by filling with chlorin chambers the floors of which are covered with dry-slaked lime: $CaH_2O_2 + Cl_2 = H_2O + CaCl_2O$. The reaction is not complete, and part of the lime remains unchanged. Theoretically the compound should contain 48.9 per cent of chlorin, but practically only 25 to 40 per cent is available. This compound, Cl—O—Ca—Cl, is intermediate between calcium chlorid, Cl—Ca—Cl, and calcium hypochlorite, Cl—O—Ca—O—Cl.

Chlorid of lime is a light white powder with a chlorous odor and a strongly alkaline and bleaching action. It is unstable, the decomposition being hastened by sunlight and heat. It should be kept in a cool, dark place. Its usefulness depends upon the ease with

which it gives up chlorin and upon its characteristic reactions, some of which are as follows:

1. Water converts it into $CaCl_2$ and $CaCl_2O_2$; or ionizes it thus:

$$CaCl_2O = Ca\cdot\cdot + Cl' + ClO'.$$
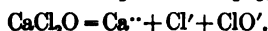
2. Dilute acids set the chlorin free either partly or wholly:

$$CaCl_2O + 2HCl = CaCl_2 + H_2O + Cl_2.$$

3. When boiled with water, a strong solution yields oxygen and a weak solution calcium chlorate:

$$CaCl_2O = CaCl_2 + O. \quad 6CaCl_2O = Ca(ClO_3)_2 + 5CaCl_2.$$

It is by the last reaction that it is used in the preparation of potassium chlorate, the calcium being replaced by potassium.

4. In contact with the higher oxids of cobalt, manganese, iron, and copper the oxygen is expelled, and in this way chlorid of lime may be used as a source of oxygen.

5. On warming it with ammonia, nitrogen is liberated:

$$3CaCl_2O + 2NH_3 = 3CaCl_2 + 3H_2O + 2N.$$
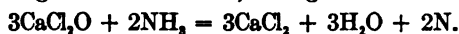
Chlorid of lime is used for many purposes, but particularly as a disinfectant, an antiseptic, an oxidizer, a source of chlorin, and as a bleaching agent. The cloth to be bleached is dipped in the chlorid solution and then in a dilute acid. The chlorin set free in the meshes of the cloth oxidizes the coloring matter.

Calcium Sulfid, CaS, is obtained by reducing the sulfate with carbon or hydrogen, or by heating lime in hydrogen sulfid or carbon disulfid. It is a waste product of the manufacture of soda according to the Le Blanc process. It is a white or pale-yellow solid, almost insoluble in water, and has the odor of hydrogen sulfid. It phosphoresces in the dark after having been exposed to the light. This property seems to be due to the presence of minute quantities of sulfids of other metals, as bismuth and magnesium. The same property is seen in barium sulfid.

Calcium Hydrosulfid, CaH_2S_2, is obtained by the action of warm water upon calcium sulfid, or by passing hydrogen sulfid through water containing calcium sulfid in suspension. It is only known in solution and is decomposed by heat. It has the property of softening hair and changing it to a gelatinous mass, and has been used by the orientals for softening the hair and beard with a view to its easy removal.

Calcium Disulfid, $CaS_2,3H_2O$, is obtained in the form of yellow crystals by boiling milk of lime with sulfur.

Calcium Polysulfids.—When calcium sulfid, or calcium hydroxid, is boiled with water and sulfur, a yellow solution of CaS_4 and CaS_5 is obtained. Upon adding an acid to the solution, sulfur separates in the finely-divided state called *milk of sulfur.*

Calcium Selenid, CaSe, is a white solid obtained by igniting calcium selenate, CaSeO$_4$.

Calcium Phosphid, Ca$_3$P$_2$, is prepared by heating together calcium and phosphorus away from the air. It is a dark, unstable solid which is decomposed by water with the evolution of hydrogen phosphid, H$_3$P.

Calcium Carbid (Calcium Acetylid), CaC$_2$, is prepared by the action of carbon upon lime at the temperature of the electric furnace (3000°): CaO + 3C = CO + CaC$_2$.

Pure calcium carbid forms crystals which are nearly colorless. The commercial substance has a dark-green or steel-gray color and smells of acetylene and hydrogen phosphid. It has a specific gravity 3.22, and melts only at a white heat. It decomposes water with the evolution of acetylene gas, C$_2$H$_2$. It is now manufactured in quantities and much used as a source of acetylene for lighting purposes.

Calcium Salts are obtained by dissolving the oxid or hydroxid in dilute acids, or by decomposing the salts of the heavy metals with calcium hydroxid. They represent nearly all the acids, and there are many double and a few basic salts. They are generally soluble in water, the more important exceptions being the arsenite, fluorid, carbonate, phosphate, sulfate, sulfite, and oxalate, and most silicates. All except calcium fluorid are soluble in dilute acids. There is but one series, since only bivalent calcium makes salts.

Calcium Chlorate, Ca(ClO$_3$)$_2$, is a white crystalline salt formed by heating a dilute solution of bleaching powder, 6CaCl$_2$O = Ca(ClO$_3$)$_2$ + 5CaCl$_2$.

Calcium Sulfite, CaSO$_3$,2H$_2$O, is a white powder obtained by mixing in solution a calcium salt with a normal sulfite. A solution of this salt in sulfurous acid, obtained by passing sulfurous oxid into milk of lime, is used in the manufacture of beer, being added to the cask to act as an antiseptic.

Calcium Sulfate, CaSO$_4$, occurs as the mineral anhydrite in rhombic prisms. Gypsum, alabaster, and selenite are various forms of CaSO$_4$,2H$_2$O, and crystallize in monoclinic prisms. Calcium sulfate is obtained artificially by treating calcium chlorid with sulfuric acid or a soluble sulfate. It forms a fine, white, crystalline precipitate, which is hydrous like gypsum. It is found in natural waters and constitutes the permanent hardness.

Calcium sulfate has a specific gravity 2.3, loses its water of crys-

tallization when heated, is slightly soluble in water (1 part in 400), and dissolves in acids. When boiled with sulfuric acid and cooled, the acid sulfate, $H_2SO_4,CaSO_4$, crystallizes out. It is used as a fertilizer, in the manufacture of plaster of Paris, and as a filling for writing-paper. Alabaster is used for works of ornament and art. The sculptures and bas-reliefs of the ancient Assyrian and Babylonian palaces were made in alabaster.

Plaster of Paris.—When gypsum is heated to 110° it loses about three fourths of its water of crystallization and becomes the white powder called *plaster of Paris*. When this is mixed with water it unites with it again, becoming a rigid solid. Because of this property it is used as a cement and as material for plaster casts and moulds. It hardens or sets in a quarter or half an hour. If the gypsum is too strongly heated (200°) it loses the whole of its water, is said to be *dead burnt*, and hardens slowly and imperfectly.

Potassium Calcium Sulfate, $K_2Ca(SO_4)_2,H_2O$, is formed when potassium and calcium sulfates are mixed with the requisite amount of water. The mass becomes quickly solid. It takes a good polish and may be used for casts instead of gypsum.

Sodium Calcium Sulfate, $Na_2Ca(SO_4)_2$, occurs as the mineral *glauberite*.

Calcium Nitrate, $Ca(NO_3)_2$, is formed by dissolving calcium salts in nitric acid. It is a white deliquescent solid, which crystallizes from solution with $4H_2O$. It is constantly formed in calcareous soils by the agency of certain bacteria, and it forms an incrustation on the walls of cattle-stalls, hence the name *wall saltpeter*.

Calcium Phosphates.—The normal calcium phosphate, $Ca_3(PO_4)_2$, is a constituent of many rocks, and is found in more or less impure masses called *phosphate beds*. It is the principal constituent of bones and an important food of both plants and animals. It is insoluble in water, but soluble in acids. It is thrown down by ammonia from its acid solutions as a white gelatinous precipitate, or by adding sodium phosphate to an ammoniacal solution of calcium chlorid.

The acid calcium phosphates, $CaH_4(PO_4)_2$ and $CaHPO_4$, are formed by the action of acids upon the normal phosphate. The former is easily soluble in water, while the latter is not. When these are heated they are converted first into the pyrophosphate, $Ca_2P_2O_7$, and then into the metaphosphate, $Ca(PO_3)_2$.

Phosphate Fertilizers.—The presence of phosphoric acid or soluble phosphates in soils is necessary to their fertility. · Soils deficient in these are enriched by addition of a phosphate fertilizer. The native normal calcium phosphate is insoluble in water and may be abundant even in a sterile soil. It is rendered soluble by treatment with sulfuric acid whereby a mixture of the acid calcium phosphate, $CaH_4(PO_3)_2$, and calcium sulfate, $CaSO_4$, is obtained. This is called *superphosphate of lime,* and is manufactured and used in large quantities as a fertilizer.

Calcium Carbonate, $CaCO_3$, occurs massive as *limestone,* crystallized in rhombohedrons as *calcite,* and in rhombic prisms as *aragonite,* in crystalline masses as *marble,* in amorphous or semicrystalline masses as *travertine* and *stalactites,* and in beds of fine-grained material, the shells of microscopic animals (foraminifera), as *chalk.* It is the essential constituent of shells, corals, and pearls, and is found in the bodies of plants and animals generally. It may be obtained artificially by treating calcium chlorid with a soluble carbonate. The precipitate is first amorphous, but presently becomes crystalline, calcite when cold, aragonite when boiled.
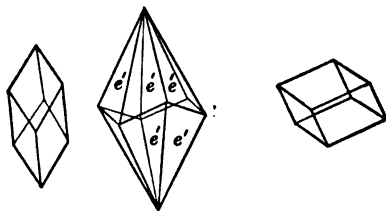
Fig. 78.—Crystals of Calcite.

Calcium carbonate is almost insoluble in pure water, but dissolves somewhat in the presence of carbon dioxid, probably changing to the hydrocarbonate $CaH_2(CO_3)_2$. One liter of water saturated with carbon dioxid will dissolve 0.7 gram of $CaCO_3$. If the solution be allowed to stand, crystals separate having the composition $CaCO_3,5H_2O$. Natural waters which contain from·5 to 30 parts to 100,000 are called *hard waters* or *limestone waters.* The salt is precipitated by boiling the water, and it constitutes the *temporary hardness.* It dissolves in acids, carbon dioxid being evolved with effervescence. It decomposes when heated and at 600° the dissociation is complete. On cooling the parts reunite: $CaCO \rightleftharpoons CaO + CO$.

Of the two native allotropes, aragonite is the less stable, changing at 300° to calcite and falling to powder. Calcite has specific gravity 2.71, aragonite 2.94. Very pure crystals of calcite, called *Iceland spar,* show double refraction and are used in optical instruments.

The various forms of calcium carbonate find numerous applications in the arts. Limestone is used for building, as a flux in iron smelting, in the manufacture of lime. Marble and the purer limestones are used as fine building material, for statuary, and in the manufacture of glass. Chalk is used for writing-crayons and in the manufacture of cements.

Calcium Silicates.—Calcium is a constituent of nearly all native silicates, some of which are almost pure calcium silicate. Examples are *wallastonite,* $CaSiO_3$, *okenite,* $CaH_2Si_2O_6,H_2O$, *gurolite,* $Ca_2H_2Si_3O_9,H_2O$, and *apophyllite,* $4CaH_2Si_2O_6,KF,4H_2O$.

Glass.—Glass is essentially an amorphous mixture or mutual solution of calcium (or lead) and alkali silicates. It is made by fusing together quartz sand, calcium (or lead) carbonate, and an alkali carbonate. Other metals, as well as boric and phosphoric acids, are added for special purposes. An excess of the alkali renders the glass softer, more fusible, and more soluble. Glass may be moulded or blown or worked with the blowpipe.

Pure glass is colorless. Colors are obtained by adding metallic oxids; uranium or antimony for yellow, cobalt for blue, iron or chromium for green, iron or copper for red, manganese for violet, phosphoric acid or calcium fluorid for opaque white.

Glass which has been cooled rapidly from fusion is very brittle. When melted glass is dropped into water, the parts are left under such high tension that upon the slightest fracture of the surface the whole flies to pieces. Examples are seen in Prince Rupert drops. To render the glass less brittle, it is *annealed* by allowing it to cool very slowly. A tough glass is made by annealing in oil.

Sodium glass, sodium-calcium silicate, is comparatively fusible, soft, and soluble especially in alkalies. It is cheap and easily worked and is used for window glass, plate glass, and ordinary bottles. It is known as *crown glass.*

Potassium glass, potassium-calcium silicate, is harder, less fusible, and less soluble than sodium glass. It is called *Bohemian glass* and is used for chemical apparatus and combustion-tubing.

Flint glass or *lead glass* is a potassium-lead silicate, lead taking the place of calcium. It has a high refractive power, and takes a fine polish. It is used for lenses and for the fancy-ware known as cut glass.

Thallium flint glass, thallium-lead silicate, contains thallium instead of potassium. It is more highly refractive than flint glass.

Strass or *Paste* is a flint glass rich in lead which is so brilliant and highly refractive that it closely resembles the diamond, from which it is most easily distinguished by its inferior hardness. It is used for artificial gems.

If molten glass is cooled too slowly, small crystals are formed, and it loses more or less of its transparency. This is called *devitrification,* and may take place in cold glass if sufficient time is allowed. Thus very old glass is sometimes white and semi-opaque.

Glass Manufacture.—Glass was made in Egypt two thousand years before Christ. The manufacture gradually spread to Greece, Rome, and Venice. The Venetian colored glass was already famous in the sixteenth century. Stained-glass windows were used in Limoges in 979 A.D.

In making glass the finely ground materials are thoroughly mixed and placed in a fire-clay pot along with a little broken glass to assist the melting. The charge is heated in a furnace of special design to quiet fusion, or until all gases (CO_2, SO_2, and O) are expelled.

The quantities of materials used for some typical glasses are as follows (Thorpe's Indust. Chem.):

	SiO_2	Na_2CO_3	Na_2SO_4	$CaCO_3$	CaO	MnO_2	Pb_3O_4	K_2CO_3	Coke
French Plate....	100	34	......	14.5	.....	0.25			
Bohemian.......	100	......	......	......	18	.....	.....	40	
Window........	100	5	37.5	35.8	.....	0.4	.....	.....	4
Lead Flint......	100	......	......	......	.....	.....	60	20	
Bottle.	100	......	25	34	.....	.....	.....	.....	3

Plate glass is cast on an iron plate or table and brought to a uniform thickness with a heavy iron roller. After being annealed, the plate is ground to a perfectly plane surface with sand and water, then polished with leather rubbers covered with emery-dust or putty-powder.

Window-glass is blown. A ball of the semi-fused pasty glass is taken on the end of an iron tube, and, by blowing through the tube, first a globe, then a cylinder, is formed. The latter is cut longitudinally and allowed to spread out on a table. The edges are trimmed, the glass annealed, and the sheet finally cut into proper sizes for the market.

Cut-glass ware is blown or moulded to the general shape, then cut on an emery-wheel and polished with rouge (iron oxid) or putty.

Most of the plain glassware, such as bottles, tumblers, dishes, and lamp-chimneys, are made by blowing the glass into a mould or pressing it into a die, much of the work being done by machinery.

Calcium Oxalate, CaC_2O_4, though an organic salt, deserves mention here. It falls as a white crystalline precipitate when ammonium oxalate, $(NH_4)_2C_2O_4$, is added to a neutral solution of a calcium salt. It is almost insoluble in water, and is used for the separation and determination of calcium.

STRONTIUM.

Symbol Sr. Atomic weight 87. Valence II and IV. Specific gravity 2.5. Melting-point about 700°.

Occurrence.—The principal native compounds of strontium are *celestite*, $SrSO_4$, and *strontianite*, $SrCO_3$. Strontium occurs also in small quantities associated with limestones and various silicates and as chlorid and sulfate in salt waters.

History.—In 1790 Crawford suggested the presence of a peculiar earth in strontianite. In 1791 Hope and in 1792 Klaproth verified the suggestion. Davy prepared the metal by electrolysis in 1808. The name is from Strontian, a village of Argyllshire.

Preparation.—Strontium is prepared by electrolysis of the chlorid or hydroxid; or by the action of sodium amalgam upon strontium chlorid, whereby strontium amalgam is formed from which the mercury is removed by distillation in a current of hydrogen.

Properties.—Strontium is a yellow metal of specific gravity 2.5 and somewhat harder than calcium, which it much resembles. It oxidizes in the air and decomposes water vigorously, When heated it burns in air, oxygen, carbon dioxid, and in vapors of bromin, iodin, and sulfur. It decomposes water slowly, dissolves in acids, and

reduces silicic oxid and silicates. It colors the flame crimson and has a characteristic spectrum.

STRONTIUM COMPOUNDS.

Strontium is chemically active and forms numerous compounds exactly analogous to those of calcium. Its valence is two, though in a few compounds it acts as a tetrad. It is strongly basic, showing no acid properties at all. Its compounds are mostly electrolytes and partially dissociate in solution with the free, colorless, positive ion, $Sr^{..}$.

The thermal relations of strontium are shown by the following equations:

(Sr,O) $= 128,400$ c. $(Sr,H_2,O_2) = 214,500$ c. (Sr,S) $= 97,400$ c.
$(Sr,S,O_4) = 330,900$ c. $(Sr,N_2,O_6) = 209,800$ c. $(Sr,C,O_3) = 281,200$ c.
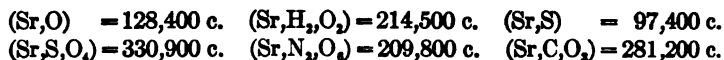
All these except the nitrate develop heat on solution in water.

Strontium Fluorid, SrF_2, is a white crystalline powder prepared by action of hydrogen fluorid upon strontium oxid or carbonate.

Strontium Chlorid, $SrCl_2$, is obtained by burning strontium in chlorin or by dissolving strontium carbonate in hydrochloric acid. Long hexagonal efflorescent needles of $SrCl_2,6H_2O$ separate from the solution. They have a bitter taste and a specific gravity 1.6.

· **Strontium Bromid,** $SrBr_2$, is obtained by heating strontium in bromin or by dissolving strontium carbonate in hydrobromic acid. It crystallizes with $6H_2O$.

Strontium Iodid, SrI_2, is a white solid obtained by dissolving the carbonate in hydriodic acid. It crystallizes with $6H_2O$.

Strontium Oxid, SrO, is obtained by heating the hydroxid, carbonate, or nitrate; or by decomposing the carbonate by means of superheated steam. It is a white, porous, infusible solid which slakes with water like lime, forming the hydroxid. It dissolves readily in acids.

Strontium Hydroxid, SrH_2O_2, is formed by union of strontium oxid with water. It is a light white powder, more soluble in water than lime; 100 parts dissolve 2 parts when cold and 42 parts when boiling. It crystallizes from the solution with $8H_2O$. It is prepared in quantities by the action of sodium hydroxid upon strontium sulfid, $SrS + NaHO + H_2O = NaH_2S_2 + SrH_2O_2$. It is strongly alkaline and dissolves in nearly all the acids to form salts.

In solution it dissociates partially into the strontium_ ions and hydroxyl ions.

Strontium hydroxid is used in the manufacture of beet sugar. It forms a strontium saccharate which is easily decomposed by carbon dioxid.

Strontium Dioxid, SrO_2, separates as a crystalline hydrate, $SrO_2,8H_2O$, upon addition of hydrogen peroxid to solution of strontium hydroxid. It looses the water when gently heated, and at red heat parts with half the oxygen.

Strontium Sulfid, SrS, is obtained by direct union or by reducing the sulfate with carbon. It is a white powder which dissolves in water to form both the hydroxid and the hydrosulfid:

$$SrS + 2H_2O = SrH_2O_2 + SrH_2S_2.$$

When strontium sulfid is boiled with sulfur and water the polysulfids, SrS_4 and SrS_5, are formed.

Strontium Salts.—Strontium forms definite salts with nearly all the acids, acting always with the valence two.

Strontium Sulfate, $SrSO_4$, occurs native as celestite in rhombic crystals and fibrous masses. It is prepared by the action of sulfuric acid upon strontium salts. It is slightly soluble in cold water, less so in hot water. It is converted by alkali carbonates into strontium carbonate, differing from barium sulfate, which is not thus changed. With strong sulfuric acid it forms the acid sulfate $SrH_2(SO_4)_2$, similar to the corresponding calcium compound.

Strontium Nitrate, $Sr(NO_3)_2$, is obtained by dissolving the carbonate in nitric acid. From concentrated solution it separates anhydrous in regular octahedrons, but from dilute solutions efflorescent, monoclinic crystals of $Sr(NO_3)_2,4H_2O$ are obtained. When combustibles are mixed with it they burn with the crimson strontium flame. It makes the pyrotechnic red fire.

Illustration.—To show the strontium-flame add a little strontium nitrate to a mixture of potassium chlorate and sugar and set on fire.

Strontium Carbonate, $SrCO_3$, occurs as strontianite in rhombic crystals. It is precipitated as a white amorphous powder when an alkali carbonate acts upon a strontium salt. It is decomposed by heat, but not quite so easily as calcium carbonate. It dissolves in the acids and serves as the most convenient material for the preparation of strontium compounds.

BARIUM.

Symbol Ba.   Atomic weight 137.4.   Valence II.   Specific gravity 3.6.   Melting-point 600°.

Occurrence.—The principal native compounds of barium are *barytes* or *heavy spar*, $BaSO_4$, often associated with lead ores; *witherite*, $BaCO_3$; and double carbonates and sulfates of barium, calcium strontium, and manganese.   It is also a constituent of many silicates and is found in sea- and mineral-waters.

History.—In 1602 a Bolognese shoemaker, V. Casciorolus, observed that heavy spar became phosphorescent when ignited with a combustible.   In 1774 Scheele discovered a new earth which Gahn showed afterwards to be found in heavy spar.   Davy obtained the metal by electrolysis in 1808.   The name is from the Greek word *barus*, which means *heavy*, and was suggested by Guyton de Morveau.

Preparation.—Barium is obtained with more difficulty than any other element of this group, and it is doubtful whether it has yet been separated in the pure state.   It is prepared by electrolysis of the chlorid or by treating the chlorid with sodium amalgam and decomposing the barium amalgam by heating it in a stream of hydrogen.

Properties.—Barium is a yellow metal of specific gravity 3.6. It melts at red heat, but is not volatile.   It tarnishes in the air, decomposes water, and dissolves in the acids.   It cannot be prepared on a large scale and has no use in the arts.   It is recognized by its insoluble sulfate.

BARIUM COMPOUNDS.

Barium is chemically the most active member of its group.   It forms numerous compounds, acting generally with a valence II.   It imparts a pale yellowish-green color to a flame and has a characteristic spectrum.   Its compounds are best obtained from the sulfid, since the sulfate and carbonate are insoluble.   All soluble barium compounds are poisonous and the solutions contain the bivalent positive ion $Ba^{..}$.   Some barium compounds, especially the sulfid, exhibit radio-activity, that is, emit invisible rays which act upon photographic plates.

Some of the thermal equations are as follows:

$(Ba,O) = 124,200$ c.	$(Ba,O_2) = 141,600$ c.	$(Ba,S) = 98,300$ c.
$(Ba,H_2,O_2) = 214,900$ c.	$(Ba,Cl_2) = 194,700$ c.	$(Ba,Br_2) = 170,000$ c.
$(Ba,S,O_4) = 338,100$ c.	$(Ba,N_2,O_6) = 178,700$ c.	$(Ba,C,O_3) = 283,400$ c.
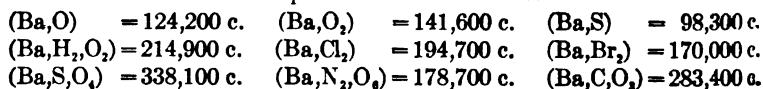
The heat of solution is generally positive, but in a few cases negative:

$$(BaO,Aq.) = 34,500 \text{ c.} \quad (Ba(NO_3)_2,Aq.) = -9,400 \text{ c.}$$
$$(BaClO_3,Aq.) = -6,700 \text{ c.}$$
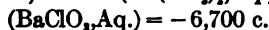
Barium Fluorid, BaF_2, is a white crystalline solid obtained by the action of sodium fluorid upon barium nitrate or hydrogen fluorid upon barium oxid.

Barium Chlorid, $BaCl_2$, is formed by the action of hydrochloric acid upon the oxid, sulfid, or carbonate of barium. It is a white crystalline solid forming rhombic tables of composition $BaCl_2,2H_2O$, which lose the water of crystallization at 113°. It dissolves about one part in two of water, but is almost insoluble in hydrochloric acid and alcohol. It melts at red heat, and the fused salt is alkaline because of the formation of a little barium oxid. It has a bitter taste and is poisonous.

Barium Bromid, $BaBr_2$, is formed by the action of hydrogen bromid upon barium hydroxid or barium sulfid. It is a white solid, crystallizing with $2H_2O$, one half of which it loses at 75° and all at 100°.

Barium Iodid, BaI_2, is obtained by the action of hydrogen iodid upon barium hydroxid or sulfid. It is a white solid which forms various hydrates.

Barium Oxid, BaO, is obtained by burning barium, or by igniting the nitrate, or by reducing the carbonate with carbon. Small quantities may be prepared by igniting the iodate, $Ba(IO_3)_2 = I_2 + 5O + BaO$. It is a heavy white crystalline mass which has specific gravity 4.73 and melts at red heat. On contact with water it slakes vigorously, becoming red-hot. When heated in the air it takes oxygen and becomes BaO_2.

Barium Hydroxid, BaH_2O_2, is obtained by union of barium oxid and water or by reducing the carbonate with superheated steam: $BaCO_3 + H_2O = CO_2 + BaH_2O_2$. It is a loose white powder which melts at a low red heat and cools to a crystalline mass of specific gravity 4.5. It dissolves in water in increasing quantities as the temperature rises, 3.5 parts at 20° and 90 parts at 100° in 100 parts. The solution is called baryta-water, is more alkaline than lime-water, and absorbs carbon dioxid, precipitating barium carbonate, $BaCO_3$. It crystallizes from solution as $BaH_2O_2,8H_2O$, which is efflorescent, losing $7H_2O$ on exposure to the air. It is wholly basic, dissolving in the acids to form salts.

Barium hydroxid is much used as an alkali in analytical processes, being specially adapted for certain actions, since the excess is easily removed as carbonate or sulfate.

Barium Dioxid (Peroxid), BaO_2, is obtained by heating the oxid or hydroxid to 450° in dry oxygen or in air free from carbon dioxid. It is a white powder which loses half its oxygen at red heat. It forms the hydrate $BaO_2,8H_2O$, which loses its water at 130°, and which may be formed directly by action of hydrogen peroxid upon barium hydroxid: $BaH_2O_2 + H_2O_2 + 6H_2O = BaO_2,8H_2O$. It dissolves in acids to form the ordinary barium salts. It is used in the preparation of hydrogen peroxid.

Barium Sulfid, BaS, is obtained by heating barium oxid in a stream of hydrogen sulfid or by reducing barium sulfate with carbon. It is a white powder which forms the crystalline hydrate $BaS,6H_2O$, and which acts with water to form the hydroxid and hydrosulfid $BaS + 2H_2O = BaH_2O_2 + BaH_2S_2$.

Barium Hydrosulfid, BaH_2S_2, is obtained as above or by passing hydrogen sulfid through solution of BaS or BaH_2O_2.

Barium Polysulfids.—By action of sulfur upon barium sulfid the polysulfids, BaS_2, BaS_4,H_2O, and BaS_5 may be formed.

Bononian Phosphorus.—Phosphorescent barium sulfid may be prepared by mixing 5 parts precipitated barium sulfate and 1 part carbon and igniting for ten or fifteen minutes. The mixture is placed in tubes while hot and sealed. On exposure to sunlight or magnesium light it phosphoresces in the dark, with an orange-colored light. This is called *Bononian* or *Bolognian phosphorus,* after the Bolognese shoemaker who first prepared it.

Barium Salts.—Barium and its oxid and hydroxid are soluble in most acids, and nearly all the theoretical salts have been prepared. Only a few of them are soluble in water, but most of them dissolve in acids. They are generally isomorphous with the calcium salts.

Barium Chlorate, $Ba(ClO_3)_2$, is obtained in monoclinic prisms by the action of chloric acid upon barium carbonate.

Barium Iodate, $Ba(IO_3)_2$, is obtained by action of barium chlorid upon potassium iodate as a white granular solid slightly soluble in water.

Barium Sulfite, $BaSO_3$, is precipitated from barium solutions by sulfite ion as a white powder, soluble in hydrochloric acid.

Barium Sulfate, $BaSO_4$, occurs native as heavy spar in white rhombic prisms. It is precipitated from barium solutions by sulfuric acids or soluble sulfates as a white powder of specific

gravity 4.5. It is almost insoluble in water, one part requiring 400,000 parts of water. It is slightly soluble in acids. Heated with sulfuric acid and cooled, it forms crystals of $BaH_2(SO_4)_2$ with or without $2H_2O$.

Barium sulfate is much used as an adulterant of white lead and as a constituent of mixed paints, and also as a weighting material for cards and paper.

Barium Disulfate, BaS_2O_7, is formed as a white precipitate by the action of disulfuric acid upon barium sulfate.

Barium Selenate, $BaSeO_4$, is a white solid obtained by action of barium chlorid upon alkali selenates.

Barium Nitrate, $Ba(NO_3)_2$, is prepared by action of barium chlorid upon alkali nitrates or by action of nitric acid upon barium carbonate or sulfid. It crystallizes from solution in mixed cubes and octahedrons, has specific gravity 3.2, and melts at 597°. Its solubility increases with the temperature, 100 parts of water dissolving 9 parts at 20°, 17 at 50°, and 32 at 100°. When strongly heated it decomposes, leaving BaO.

Barium nitrate is used for the green fire in pyrotechny and in the manufacture of the explosive called *saxifragin*, which contains 76 parts barium nitrate, 22 parts carbon, and 2 parts potassium nitrate.

Barium Phosphates.—The normal salt, $Ba_3(PO_4)_2$, the two acid salts, $BaHPO_4$ and $BaH_4(PO_4)_2$, and various double salts have been prepared.

Arsenates and antimonates of barium are similar to phosphates.

Barium Carbonate, $BaCO_3$, occurs as witherite in rhombic prisms and pyramids isomorphous with aragonite. It is obtained by adding ammonium carbonate to solution of barium chlorid, as a dense white precipitate soluble in 14,000 parts of water. It fuses at red heat, loosing a portion of the CO_2 and becoming alkaline. It furnishes the most convenient material for the preparation of barium compounds and is used as a rat poison.

Barium Silicates.—Barium is a constituent of a number of native silicates. The normal salt, $BaSiO_3$, may be obtained as a white precipitate by adding barium chlorid or nitrate to dilute solution of sodium silicate, Na_2SiO_3.

Barium Fluosilicate, $BaSiF_6$, is thrown down in fine crystals when fluosilicic acid acts upon a soluble barium salt.

CHAPTER XXXV.

GROUP II B. THE ZINCOIDS. ZINC GROUP.

Zinc 65.4. Cadmium 112.4. Mercury 200.

ZINC, cadmium, and mercury are metallic in both physical and chemical properties, but zinc is less basic than the others and is even acidic in a few compounds.   As the atomic weight increases the specific gravity increases, but the melting and boiling temperatures diminish.   They dissociate when volatilized, so that the molecule contains but one atom, as is shown by the fact that the vapor density and the atomic weight are practically the same.   Zinc and cadmium are usually associated together and are much alike.   Mercury is peculiar in that it is the only metal liquid at the ordinary temperature, and that it forms no hydroxid.   They are all bivalent, but mercury acts also as a pseudo monad.

The following table exhibits some leading physical properties:

	Atomic Weight.	Specific Gravity.	Melting-point.	Boiling-point.
Zinc............	65	7.16	420°	927°
Cadmium	112	8.65	317°	772°
Mercury	200	13.6	− 39°	357°

ZINC.

Symbol Zn.   Atomic weight 65.4.   Valence II.   Specific gravity 7.0. Melting-point 420°.   Boiling-point 950°.

Occurrence.—Zinc has been found free·in small quantities in Australia.   Its principal ores are *smithsonite*,· $ZnCO_3$, *zinc blende* ZnS, *calamine*, Zn_2SiO_4,H_2O, *zincite*, ZnO, *gahnite*, $ZnAlO_4$, and mixed compounds of zinc with lead, iron. copper, etc.   Traces of zinc are found in some waters and in the plant and animal bodies. Zinc is found in nearly all countries, but is particularly abundant in association with the lead of Missouri, Wisconsin, Iowa, and Illinois.

History.—The alloy of zinc and copper, called *brass*, was known to the ancients, but zinc was not recognized as a distinct metal until the time of Paracelsus, in the sixteenth century.   The name was first used by Valentine in the fifteenth century.   Zinc of reasonable purity was prepared by Henckel in 1720.

Preparation.—Pure zinc is prepared by reducing the artificial carbonate with carbon: $2ZnCO_3 + C = 3CO_2 + 2Zn$.

Zinc is extracted from its ores by a double process of oxidation and reduction.   The ores most used are the carbonate and the sulfid.   They are first roasted, whereby the carbonate is decomposed, $ZnCO_3 = CO_2 + ZnO$, and the sulfid oxidized, $ZnS + 3O = SO_2 + ZnO$.   The oxid thus obtained is mixed with coke and heated to redness.   The zinc distils and is condensed in iron receivers.   The receivers contain, besides the fused zinc, a gray powder called *zinc dust*, a mixture of zinc and zinc oxid..

Physical Properties.—Zinc is bluish-white, brittle, moderately hard, melts at 420°, and boils at 950°.   The vapor has a density equal to one half the atomic weight, and the molecule is therefore monatomic.   It crystallizes in hexagonal prisms and pyramids of specific gravity 7.0 to 7.2.   At 100° it is malleable and ductile, but at 300° it is again brittle and may be pulverized.   After being rolled or drawn it is no longer brittle when cold.   It expands as it solidifies and makes sharp castings.   Its specific heat is 0.093.

Chemical Properties.—Zinc tarnishes in moist air, becoming covered with a thin layer of basic carbonate, and when heated burns with a white flame to zinc oxid.   Hot water is decomposed by zinc-dust and the zinc-copper couple (made by letting zinc stand for a time in a solution of copper sulfate).   It dissolves in alkali hydroxids and dilute acids, evolving hydrogen.   It acts violently upon nitric acid, decomposing it, and forming, besides zinc nitrate, oxids of nitrogen and ammonia.   Pure zinc is scarcely attacked by strong acids, the surface becoming covered with a layer of condensed hydrogen, which protects the metal.

Uses.—Zinc is used in sheets for various domestic purposes, for galvanizing iron, for negative electrodes in galvanic batteries, as a reagent in laboratories, and in the manufacture of various alloys, of which brass is the most important.   Zinc-dust is used as a reducing agent and as a paint for iron articles.   Iron is galvanized by dipping it in melted zinc.   The zinc covers the surface of the iron with a film not easily attacked by the atmosphere.

Alloys of Zinc.—Zinc forms homogeneous alloys with some metals, as tin, copper, silver, and antimony, while with others, as lead and bismuth, it fuses in all proportions, but on cooling separates, each metal retaining a definite amount of the other. It is to this property that is due its use in desilverizing lead. For composition of the alloys see under Copper.

COMPOUNDS OF ZINC.

Zinc is chemically quite active and its compounds are numerous. It is bivalent and mostly basic, though with strong alkalis it has a weak acid character and forms zincates. It yields the bivalent positive ion $Zn^{..}$, which is colorless and poisonous.

The heat of formation of a few compounds is as follows:

$(Zn,O) = 85,800$ c. $(Zn,H_2,O_2) = 151,100$ c. $(Zn,S,O_4) = 230,000$ c.
$(Zn,Cl_2) = 97,200$ c. $(Zn,Br_2) = 76,000$ c. $(Zn,I_2) = 49,200$ c.
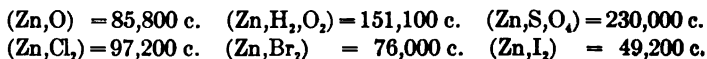
All these compounds develop heat in dissolving in water.

Zinc Fluorid, ZnF_2, is obtained by heating zinc oxid in a stream of hydrogen fluorid as colorless monoclinic needles of specific gravity 4.48. It forms with water several hydrates.

Zinc Chlorid, $ZnCl_2$, is prepared by the action of chlorin upon zinc, or of hydrochloric acid upon zinc or its compounds, or by distilling together zinc sulfate and calcium chlorid. It is a soft, white, deliquescent solid which melts at 100° and distils at 680°. It forms a caustic solution in water from which crystals of $ZnCl_2,H_2O$ may be separated. When the solution is evaporated it decomposes, yielding zinc oxid and hydrochloric acid and the basic chlorid $Zn(HO)Cl$. It forms double chlorids with alkali metals, as $ZnCl_2,2KCl$.

Zinc chlorid is used as a caustic in surgery, as a dehydrating agent, as an antiseptic, especially for the preservation of wood, as a help in soldering, and as a weighting material for cotton goods. A mixture of oxid and zinc chlorid sets quickly to a hard mass and has been used in filling teeth.

Zinc Bromid, $ZnBr_2$, is prepared by heating zinc and bromin vapor or by dissolving zinc hydroxid in hydrobromic acid. It forms white deliquescent needles.

Zinc Iodid, ZnI_2, is prepared by heating the elements together or by digesting iodin in water containing suspended zinc. It forms white

octahedral crystals of specific gravity 4.7, which melt at 446° and boil at 624°. It forms double iodids with the alkali metals.

Zinc Cyanid, $Zn(CN)_2$, is obtained by precipitating zinc acetate with hydrocyanic acid. It is a white powder and is used in medicine.

Zinc Oxid, ZnO, occurs as the mineral *zincite* in red or yellow hexagonal crystals of specific gravity 5.4. The color is due to the presence of a small amount of manganese. It may be prepared by · burning zinc in the air or by igniting the carbonate or nitrate. It is a loose, flaky, white powder which was called by the alchemists *philosophers' wool.* It turns yellow when heated, but whitens again as it cools. In the oxy-hydrogen flame it does not melt, but emits an intense white light like lime, and remains for some time phosphorescent. It is insoluble in water, but dissolves in acids to form salts. It is used as a pigment called *zinc white* or *permanent white.* It does not darken in the air like white lead, since the sulfid is white.

Zinc Hydroxid, ZnH_2O_2, is precipitated from zinc solutions as a white powder. It dissolves in excess of the alkali as alkali zincate, but separates from the solution as ZnH_2O_2,H_2O in regular octahedrons. It dissolves in ammonia to form compounds of the zinc ammonium ion $Zn(NH_3)_n$, in which n may have several values. When heated it loses water, then dissociates into ZnO and H_2O.

Zinc Sulfid, ZnS, occurs as *zinc blende* crystallized in isometric forms, chiefly tetrahedrons of specific gravity about 4, or as *wurtzite* in hexagonal crystals. It may be prepared by direct union of the elements or by action of ammonium sulfid upon zinc solutions. It is a white powder insoluble in water, soluble in dilute acids except acetic. It is precipitated by hydrogen sulfid from zinc acetate solution, and this reaction serves to separate zinc from other metals. It is the only metallic sulfid which is white.

Zinc Pentasulfid, ZnS_5, is formed when potassium pentasulfid is added to a zinc solution.

Zinc Selenid, ZnSe, is obtained by heating zinc in hydrogen selenid as reddish-yellow isometric crystals.

Zinc Tellurid, ZnTe, is obtained in ruby-red isometric crystals by heating zinc in hydrogen tellurid.

Zinc Nitrid, Zn_3N_2, is a gray powder obtained by heating zincamid, $Zn(NH_2)_2$.

Zinc Phosphid, Zn_3P_2, is a gray, lustrous, metallic solid obtained by heating zinc and phosphorus together and by various other reactions.

The compounds $ZnSiF_6,6H_2O$, $ZnTiF_6$, and $ZnSnF_6,6H_2O$ have been prepared.

Zinc Salts.—Zinc salts of most of the acids are easily obtained, and there are basic carbonates, sulfates, and nitrates. They are mostly white, crystalline, and soluble. The chlorate, perchlorate, bromate, iodate, and periodates are obtained by dissolving zinc car-·bonate in the corresponding acid.

Zinc Sulfate, $ZnSO_4,7H_2O$, is prepared by dissolving zinc in sulfuric acid or by roasting zinc sulfid with free access of air. It crystallizes from the solution in rhombic prisms with $7H_2O$. The crystals effloresce and at 100° lose $6H_2O$ and at 300° become anhydrous. If the evaporation is conducted at 40° the hydrate $ZnSO_4,6H_2O$ is obtained. It is quite soluble in water, 100 parts dissolving 160 at 18° and 654 parts at 100°. It forms double salts with the alkali sulfates, as $ZnSO_4,K_2SO_4,6H_2O$, and when heated it decomposes, leaving the basic salt $ZnSO_4,2ZnO$, or $Zn {<}{\begin{matrix} O-Zn-O \\ O-Zn-O \end{matrix}}{>} SO_4$.

At white heat all the zinc sulfates are decomposed, leaving zinc oxid.

Zinc sulfate is white, has an astringent taste, is poisonous, and is used in medicine and in dyeing. The old name for sulfuric acid was *oil of vitriol*, and certain of the sulfates were called *vitriols*. The more important ones were *white vitriol*, $ZnSO_4,7H_2O$, *green vitriol*, $FeSO_4,7H_2O$, and *blue vitriol*, $CuSO_4,5H_2O$.

Zinc selenate, selenite, tungstates, and vanadates are formed by the usual reactions.

Zinc Nitrate, $Zn(NO_3)_2,6H_2O$, is formed by the action of zinc upon nitric acid. It forms deliquescent crystals which loose water and nitric acid at 100° and leave basic zinc nitrates.

Zinc forms salts with all the acids of phosphorus, viz., hypophosphites, phosphites, and ortho, meta, and pyro phosphates. It also forms similar derivatives of arsenous and arsenic acids.

Zinc Carbonate, $ZnCO_3$, occurs native as smithsonite in rhombohedrons of specific gravity 4.42. It is obtained as a white precipitate when an acid alkali carbonate ($NaHCO_3$) is added to a solution of zinc sulfate. When the normal alkali carbonate is used basic zinc carbonates are thrown down and they are more basic as the temperature is higher. The basic carbonate, $ZnCO_3,2Zn(HO)_2,H_2O$, is used in medicine under the name of *zinci carbonas*.

Zinc Silicates.—Ortho zinc silicate, Zn_2SiO_4,H_2O, occurs as the mineral *calamine* in white rhombic prisms. Zinc is also a constituent of a number of other silicates. Zinc metasilicate is obtained in rhombic crystals by action of sodium silicate upon zinc sulfate.

CADMIUM.

Symbol Cd. Atomic weight 112.4. Valence II. Specific gravity 8.6. Melting-point 317°. Boiling-point 772°.

Occurrence.—The only pure compound of cadmium found native is the sulfid CdS in the rare mineral *greenockite*. Cadmium is found in many zinc ores, the quantity reaching 5 per cent in those from Silesia and 3 per cent in some North American ores.

History.—Cadmium was discovered by Stromeyer in 1817 and about the same time by Hermann. It was named by Stromeyer *cadmia fornicum* (furnace zinc), because it was found in the zinc furnace, cadmia being the original name for zinc.

Preparation.—Cadmium is generally prepared by separation from the zinc ores. Being more volatile than zinc it comes over with the first portion of the distillate from the zinc furnace partly as the metal and partly as the oxid. It is further separated by redistillation and then reduced with carbon, or it may be dissolved in acid, precipitated as sulfid, redissolved in acid, precipitated as carbonate, and then reduced.

Physical Properties.—Cadmium is a white, malleable, ductile metal, a little harder than tin, and of specific gravity 8.6. It melts at 320° and boils at 770°, yielding a yellow vapor of disagreeable odor. Its vapor density is half its atomic weight, and its molecule is therefore monatomic. It crystallizes in regular octahedrons, and when a bar is bent it crackles like tin. Its specific heat is 0.055.

Chemical Properties.—Cadmium does not act upon water, but steam is decomposed by cadmium vapor. Cadmium tarnishes slowly in the air and burns when heated to CdO. It dissolves in dilute hydrochloric and sulfuric acids, evolving hydrogen, and with nitric acid acts like zinc. It is negative to zinc and is displaced by it from solutions.

Alloys.—Cadmium forms alloys with many of the metals, and its addition usually lowers the fusing-point. It is therefore a constituent of fusible metal. An amalgam of mercury, cadmium, and tin is used in dentistry.

CADMIUM COMPOUNDS.

Cadmium is bivalent in all its compounds and in solution yields the colorless bivalent ion $Cd^{..}$. It is wholly basic, forming no compound with the alkali hydroxids. Its compounds are very similar to those of zinc and are usually isomorphous with them. They are all poisonous. There are a few cadmium compounds in which the valence of cadmium seems to be 1.

Some of the thermal equations are as follows:

(Cd,O) = 75,500 c. (Cd,H$_2$O$_2$)   = 134,100 c. (Cd,S,Aq.) = 32,400 c.
(Cd,Cl$_2$) = 93,200 c. (Cd,Br$_2$)   = 75,200 c. (Cd,I$_2$)   = 48,800 c.
(Cd,S,O$_4$) = 221,200 c. (Cd,N$_2$,O$_6$,Aq.) = 116,100 c. (Cd,C,O$_3$) = 181,900 c.
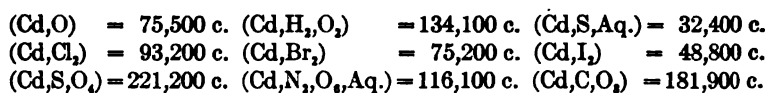
Cadmium Fluorid, CdF$_2$, is a hard white crystalline solid of specific gravity 6, formed by the action of hydrofluoric acid upon cadmium oxid.

Cadmium Chlorid, CdCl$_2$, is obtained by dissolving the metal or its oxid in hydrochloric acid. It crystallizes from the solution as CdCl$_2$,2H$_2$O in rectangular prisms of specific gravity 3.3. The crystals effloresce in the air and lose all the water when heated. It melts at 140° and sublimes in micaceous scales. It is quite soluble in water, 100 parts dissolving 140.

Cadmium Bromid, CdBr$_2$, is obtained by heating cadmium in bromin vapor or by dissolving cadmium carbonate in hydrobromic acid. It is a white crystalline soluble solid.

Cadmium Iodid, CdI$_2$, is prepared by dissolving cadmium in hydriodic acid or by digesting it with iodin and water. It crystallizes in hexagonal plates of specific gravity 5.6, melts easily, decomposes at high temperature, dissolves in equal weight of water, and is used in photography.

Cadmium Cyanid, Cd(CN)$_2$, is obtained in small white crystals by action of hydrocyanic acid upon cadmium oxid.

Cadmium Double Halids.—The cadmium halids show a strong tendency to form double salts with other halids, usually crystallizing with water from one to twelve molecules. The following are examples:

CdF$_2$,SnF$_2$,H$_2$O.   CdBr$_2$,2NaBr,5H$_2$O.
CdCl$_2$,2CaCl$_2$,12H$_2$O.   CdI$_2$,2NH$_4$I,2H$_2$O.

Cadmium Oxid, CdO, is prepared by burning the metal or by igniting the nitrate or carbonate. It is a brown or bluish-black powder composed of cubes and octahedrons of specific gravity 6.5. It is infusible even in the oxy-hydrogen flame, but is easily reduced

on charcoal, the metal burning and making a brown incrustation. It is insoluble in water, but dissolves in acids.

Cadmium Hydroxid, CdH_2O_2, is a white amorphous powder obtained by treating cadmium solutions with alkali hydroxids. It is decomposed at 300° into cadmium oxid and water.

Cadmous Compounds.—Cadmous oxid, Cd_2O, is a yellow crystalline solid, and cadmous hydroxid, CdH_2O_2, is a gray amorphous powder. They are interesting because of their similarity to the mercurous compounds.

Cadmium Sulfid, CdS, occurs native as greenockite in hexagonal prisms of specific gravity 4.9. It falls as a bright-yellow precipitate when hydrogen sulfid is added to a cadmium solution. It is soluble in strong acids, but not in ammonium sulfid, a property which distinguishes it from arsenic sulfid, which it resembles. It is used as a pigment under the name of *cadmium yellow*.

Cadmium Pentasulfid, CdS_5, is precipitated yellow from cadmium solutions by potassium pentasulfid.

Cadmium Selenid, CdSe, is a golden-yellow crystalline solid of specific gravity 8.8, and **Cadmium tellurid,** CdTe, is a black crystalline solid of specific gravity 6.2. These are both formed by direct union of the elements.

Cadmium Phosphid and **Arsenid.**—Cadmium forms alloys with phosphorus and arsenic rather than definite compounds.

Cadmium Salts.—Cadmium, cadmium oxid, and cadmium hydroxid dissolve in acids to form salts which resemble closely those of zinc. Most of the salts are soluble in water, and the solution reddens litmus, indicating hydrolysis and the presence of the hydrogen ion.

Cadmium Sulfate, $CdSO_4$, is obtained by dissolving the metal or its oxid or its sulfid in sulfuric acid. It crystallizes from the solution as $3CdSO_4,8H_2O$, and is therefore not isomorphous with zinc and magnesium sulfates, which take $7H_2O$. It, however, like them, forms double salts with the alkali sulfates. It is used in diseases of the eye. When heated it forms the basic salt $H_2Cd_2SO_6$

or $\begin{array}{l} H-O-Cd-O \\ H-O-Cd-O \end{array} > SO_2.$

Cadmium Nitrate, $Cd(NO_3)_2,4H_2O$, formed by dissolving cadmium in nitric acid, crystallizes in white deliquescent needles.

Other cadmium salts are chlorate, perchlorate, bromate, iodate, per-

iodate, sulfite, selenite, selenates, molybdates, nitrite, phosphite, phosphates, tungstates, vanadates, carbonates, silicates, borates.

MERCURY.

Symbol Hg.   Atomic weight 200.   Valence II and I.   Specific gravity 13.595.   Melting-point − 39°.   Boiling-point 358°.

Occurrence.—Mercury occurs free in small globules scattered through rocks, and especially associated with its ores.   It is also found as amalgam of gold or silver and sometimes as iodid or chlorid.   Its most important ore is *cinnabar*, HgS.   The chief localities are Idria in Austria, Almaden in Spain, California, China, Japan, and Bavaria.

History.—Theophrastus, about B.C. 300, speaks of liquid silver which may be obtained by mixing cinnabar with vinegar.   Dioscorides, in the first century, speaks of it as *hydrargyrus,water silver*,from which term we have the modern name *hydrargyrum*.   Pliny called it *argentum vivum*, which we translate *quicksilver*.   It is called *mercury* after the planet of that name.

Mercury was an object of great interest to the alchemists and early chemists.   It was extensively experimented upon in the attempts to change the baser metals into gold and silver.

Preparation.—Mercury may be separated from its ore by roasting in a reverberatory furnace, whereby the sulfur is oxidized to SO_2, while the mercury distils over and is condensed in chambers of earthenware vessels; or by distilling the ore with lime, whereby calcium sulfid and sulfate are produced and the mercury set free. The first method is the one usually employed.

The mercury thus obtained is separated from mechanical impurities by straining through chamois leather, and from other metals, which are usually tin, zinc, and lead, by distillation, best in vacuo, or by treatment with dilute acid, sulfuric or nitric.

Physical Properties.—Mercury is remarkable in being the only metal liquid at the ordinary temperature.   It is silver white and quite opaque, though in very thin films it transmits a violet blue light. Its specific gravity at 0° is 13.595.   It freezes at − 39.4° to a ductile malleable mass of octahedral crystals, at the same time contracting so that its specific gravity rises to 14.193.   It boils at 358°, yielding a colorless vapor of density about 100, a number which is half the

atomic weight and indicates that there is only one atom in the molecule.   Though its boiling-point is so high, it is volatile at all temperatures.   Its vapor tensions have been carefully measured and tabulated, and range in millimeters from 0.0002 at 0° to 0.0013 at 20°, 0.028 at 60°, 0.28 at 100°, 18.2 at 200°, 242 at 300° and 760 at 358°.   Correction must be made in barometric readings for this tension.   When subjected to changes of temperature it expands and contracts with great regularity, and this property adapts it for use in barometers and thermometers.   Its coefficient of expansion is 0.00018.   It is a good conductor of heat and electricity.

Between mercury and most solids there is capillary repulsion, so that it does not spread upon or wet the surface.   In a glass tube it presents a convex meniscus, and the column is slightly depressed by the surface tension.   When it is shaken with oil or intimately mixed with fats or many powdered solids such as sugar, sulfur, and chalk, it remains in a finely divided state.   Mercurial ointment is such a mixture.   The specific heat of mercury at 55° is 0.033.

Chemical Properties.—Mercury does not tarnish in the air and is attacked by only a few gases.   Heated in the air it slowly oxidizes to HgO, which is decomposed at a higher temperature.:

$$Hg + O \rightleftharpoons HgO.$$
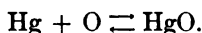
It combines directly with the halogens and sulfur.   It is not attacked by hydrochloric acid, but dissolves in warm strong sulfuric and cold nitric acids without production of hydrogen:

$$3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 4H_2O + 2NO.$$
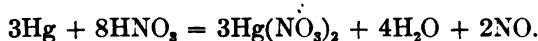
With cold dilute nitric acid mercurous nitrate, $Hg_2(NO_3)_2$, is produced.   Mercury vapor dissolves slightly in water, making it poisonous.

Illustrations.—Let fall from a considerable height a stream of water upon the surface of mercury.   Bubbles of mercury having very thin walls float upon the surface of the water and show the blue transmitted light.

To show vapor of mercury, suspend gold-leaf over mercury in a vessel. The gold gradually whitens as the amalgam forms.

Uses.—Mercury is much used in chemical and physical operations and in apparatus, notably in the barometer, thermometer, and mercury pump.   It is used in extracting gold from its ores and in making various amalgams.

Amalgams.—Mercury forms with nearly all the metals **alloys** which are called *amalgams.* Since mercury is already a liquid, the union takes place without application of heat..

Sodium and Potassium Amalgams.—Mercury unites to sodium and potassium with such vigor as to produce light and heat. These amalgams are decomposed by water, yielding hydrogen, mercury, and the alkali hydroxid. They are therefore reducing agents. When heated to 440° they form the spontaneously inflammable crystalline compounds K_2Hg and Na_2Hg.

Ammoniam Amalgam.—The so-called ammonium amalgam is obtained by treating sodium amalgam with ammonia. It is a spongy mass which soon decomposes, with separation of mercury.

Gold, silver, cadmium, and *copper* amalgams are used in filling teeth.

Zinc amalgam or amalgamated zinc is used in galvanic batteries, the mercury rendering the zinc less susceptible to the action of the acid.

Silver amalgam is obtained as arborescent needle-shaped crystals by placing a drop of mercury in a solution of silver nitrate. It is called the *silver tree* or *arbor Dianæ.*

COMPOUNDS OF MERCURY.

Mercury forms two series of compounds, mercuric and mercurous. In the former the valence of mercury is II, while in the latter it is apparently I, though the formulas are usually written so as to preserve the bivalency. So also there are two mercury ions, $H^{\cdot\cdot}$ and $Hg_2^{\cdot\cdot}$, both colorless and poisonous. Mercury forms complex ions with the halogens and with cyanogen which probably exist in the double salts. The mercuric compounds resemble those of zinc and cadmium, while the others are more nearly related to those of copper, silver, and gold.

The mercury compounds are all poisonous, but in small doses are medicinal. Taken continuously they produce salivation, affecting usually the mouth, teeth, and gums, and sometimes causing paralysis. Those most used are the two chlorids and the iodid.

Some of the thermal equations are as follows :

(Hg_2O)	$= 22,200$ cal.	(Hg,O)	$= 20,700$ cal.	(Hg,S)	$= 4,900$ cal.
(Hg_2,Cl_2)	$= 62,600$ cal.	(Hg_2,Br_2)	$= 40,500$ cal.	(Hg_2,I_2)	$= 28,400$ cal.
(Hg,Cl_2)	$= 53,200$ cal.	(Hg,Br_2)	$= 16,000$ cal.	(Hg,I_2)	$= 24,300$ cal.

Halids of Mercury.—Mercurous halids are generally insoluble in water, mercuric halids soluble. Besides these there are oxyhalids and mixed halids. Nearly every theoretical combination is realized in actual compounds. Dissociation is small, highest in the chlorid.

Mercurous Fluorid, Hg_2F_2, is a yellow crystalline powder obtained by action of hydrogen fluorid upon mercurous carbonate.

Mercuric Fluorid, $HgF_2 2H_2O$, is a white crystalline solid obtained by action of hydrogen fluorid upon mercuric oxid.

Mercuric Hydroxyfluorid, $Hg(OH)F$, is obtained as yellow crystals by decomposing mercuric fluorid at 50°.

Mercurous Chlorid, Hg_2Cl_2, occurs native as *horn quicksilver.* It is prepared as a nearly white soft powder by treating chlorin with an excess of mercury, or by treating mercurous nitrate with a chlorid, or by distilling a mixture of mercuric chlorid and mercury. It is tasteless and odorless and may be obtained in square prisms of specific gravity 7.2. It sublimes without melting, but with dissociation. It is quite insoluble in water, alcohol, and dilute acids, is decomposed by alkalis and alkali salts, and is converted by ammonia into mercurous ammonium chlorid, Hg_2NH_2Cl, ammonium chlorid in which two hydrogen atoms have been replaced by $(Hg_2)''$, or possibly amido mercurous chlorid, $Cl—Hg—Hg—NH_2$. It is unstable, gradually decomposing in the light, and hence should be kept in blue bottles. The commercial substance often contains other mercury compounds as impurities.

Mercurous chlorid is popularly known as *calomel,* a word derived from the Greek *kalomelas,* which means *beautiful black,* referring to the black color it assumes when treated with an alkali. It has been much used as a medicine, being a popular purgative and liver remedy, but its use is now on the decline because of its poisonous effects.

Mercuric Chlorid, $HgCl_2$, is commonly known as *corrosive sublimate.* It is formed by union of chlorin with heated mercury. It is prepared on a large scale by heating mercuric sulfate with common salt: $HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$. A little manganese dioxid is added to prevent the formation of mercurous chlorid.

Mercuric chlorid is a white crystalline solid soluble 7 parts in 100 of water at the ordinary temperature and 54 parts in 100 at 100°.

It is more soluble in alcohol and ether. It crystallizes in needles or rhombic prisms of specific gravity 7.2. It melts at 265° and boils unchanged at 307°. It has a harsh, metallic taste, is a violent corrosive poison, is a powerful bactericide and antiseptic.

Mercury Oxychlorids.—Several oxychlorids, or basic chlorids, of mercury are known. They are formed in various ways, most easily by boiling mercuric oxid in solution of mercuric chlorid. The crystalline bodies $HgO,2HgCl_2,H_2O$, $2HgO,HgCl_2$, and $3HgO,HgCl_2$ are examples.

Mercurous Bromid, Hg_2Br_2, is obtained by heating bromin or mercuric bromid with mercury in excess, or by heating mercurous nitrate with hydrogen bromid or an alkali bromid. It is a white powder, much resembling calomel, volatile at red heat, insoluble in water, and blackened by alkalis.

Mercuric Bromid, $HgBr_2$, is prepared by heating mercury with bromin in excess, or by dissolving mercuric oxid in hot hydrobromic acid, or by treating mercuric nitrate with potassium bromid. It forms white rhombic prisms of specific gravity 5.7, isomorphous with mercuric chlorid. It melts at 244°, sublimes unchanged, dissolves in water, alcohol, and ether, and forms double bromids and oxybromids.

Mercurous Iodid, Hg_2I_2, is formed when mercury and iodin are rubbed together in proper proportion with a little alcohol. It is also obtained by adding potassium iodid to mercurous nitrate. It is a pale-green unstable powder, is used as a medicine, and is less poisonous than mercuric iodid.

Mercuric Iodid, HgI_2, is formed by direct union or by treating a mercuric salt with potassium iodid. The precipitate is first yellow, then bright red, and is soluble in excess of potassium iodid or mercuric chlorid. It is soluble in alcohol, but not in water. It crystallizes in square octahedrons of specific gravity 6.3. It melts at 238° to a blood-red liquid and boils at 360°. It is dimorphous. The red form is converted into the yellow at 126°, but this is unstable changing back to the red variety at a touch. It forms double salts with the metallic iodids.

Mercuric Cyanid, $Hg(CN)_2$, is obtained by dissolving mercuric oxid in hydrocyanic acid. It forms white square prisms of specific gravity 4. It dissolves in 8 parts of water, but the solution is not an electrolyte and contains neither the mercury nor the cyanogen ion. It is decomposed by heat into mercury and cyanogen gas. It forms oxycyanids and numerous double compounds with other halids and metallic salts which yield the ion $Hg(CN)_4''$.

Double Halids of Mercury.—One of the remarkable characteristics of the mercury halids is the tendency to form double compounds with other halids and even with metallic salts. The following are examples of such mercuric compounds:

Chlorids.	Bromids.	Iodids.
$HgCl_2,HCl$	$HgBr_2,HBr$	HgI_2,HI
$HgCl_2,KCl,H_2O$	$HgBr_2,NaBr$	HgI_2,NH_4I
$HgCl_2,CaCl_2,6H_2O$	$HgBr_2,MgBr_2$	HgI_2,SrI_2

Mercurous halids and mercuric cyanid form similar compounds.

Mercurous Oxid, Hg_2O, is obtained by the action of alkali hydroxids upon mercurous salts. It is a black unstable powder of specific gravity 10.7. It is decomposed by heat and light and dissolves in acids to form mercurous salts.

Mercuric Oxid, HgO, is formed when mercury is long heated in the air. It is prepared by igniting the nitrate alone or with mercury. It is a red crystalline powder of specific gravity 11.14. It turns dark when heated, but becomes red again when cooled. It is very slightly soluble in water (1 part to 200,000) and decomposes at red heat. When heated with sulfur, phosphorus, or sodium it explodes. Precipitated from mercuric solutions by alkali hydroxids, it is an orange-yellow amorphous powder. It forms double compounds with the ammonium and alkali-earth chlorids. It is used in medicine under the common name of red oxid of mercury or *red precipitate.*

Mercury Hydroxids.—The hydroxids of mercury, $Hg_2H_2O_2$ and HgH_2O_2, are so unstable that they decompose at once. Thus when alkali hydroxids act upon mercury nitrates, the hydroxid which should result from the action dissociates as fast as it is formed.

Mercurous Sulfid has not been prepared. The black precipitate produced by hydrogen sulfid in mercurous solutions is a mixture of mercury and mercuric sulfid.

Mercuric Sulfid, HgS, as the mineral *cinnabar* is the chief ore of sulfur. It is found in red rhombohedral crystals and also massive. The name cinnabar was applied to it by Theophrastus, and it was called also *dragons' blood* and *Æthiops mineral.* The artificially prepared substance is known as *vermillion.*

Mercuric sulfid presents two forms, probably allotropic, the one black, the other red. The black sulfid is obtained by rubbing mer-

cury and sulfur together, or by precipitating mercuric salts with hydrogen sulfid. The precipitate is first white, then red, and finally black, the different colors being due to the formation of double salts.

The red sulfid is obtained by distilling the black sulfid or a mixture of mercury and sulfur, or by digesting the black sulfid with alkali sulfids. It is a bright-red crystalline solid, of specific gravity 8.12, insoluble in water and not readily attacked by acids. It is used in making printers' ink, in coloring sealing-wax, and as a pigment.

Sulfohalids are formed by action of a limited amount of hydrogen sulfid upon mercuric halids, $2HgCl_2 + H_2S = 2HCl + Hg_2SCl_2$, or by action of hot mercuric sulfid upon the halids.

Mercuric Selenid, HgSe, occurs in small quantities in the Hartz Mountains, accompanying lead selenid. It may be prepared by heating together and subliming mercury and selenium in gray, lustrous laminæ of specific gravity 7.1.

Mercuric Nitrid, Hg_3N_2, is prepared by heating mercuric oxid in ammonia gas at 150° until water ceases to come off:

$$3HgO + 2NH_3 = 3H_2O + Hg_3N_2.$$
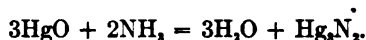
It is a very unstable brown powder, which explodes violently under the action of heat, friction, or percussion, or on contact with sulfuric acid. Alkalis decompose it with evolution of ammonia.

Mercurammonium Compounds.—Mercury combines in various ways with ammonia to form complex double halids and salts, all of which may be supposed to be derived from ammonium hydroxid by replacement of hydroxyl and hydrogen atoms. The following are examples:

Mercurous Ammonium Chlorid, $\begin{array}{c} Hg \\ | \diagdown \\ Hg \diagup \end{array} NH_2$—Cl, is a black powder obtained by action of ammonium hydroxid upon mercurous chlorid.

Mercurous Diammonium Chlorid, $\begin{array}{c} Hg{-}NH_3{-}Cl \\ | \\ Hg{-}NH_3{-}Cl \end{array}$, is a black powder obtained by action of dry ammonia upon mercurous chlorid.

Mercurous Ammonium nitrate, $\begin{array}{c} Hg \\ | \diagdown \\ Hg \diagup \end{array} NH_2$—NO₃, is obtained as a black precipitate of varying composition by action of ammonium hydroxid upon mercurous nitrate solution.

Mercuric Ammonium Chlorid, $Hg = NH_2$—Cl, falls as a white precipitate when mercuric chlorid is treated with ammonia. It is known as *infusible white precipitate.*

Dimercuric Ammonium Hydroxid, $\begin{smallmatrix}Hg\\Hg\end{smallmatrix}\!\!\diagdown\!\!\diagup N\!-\!O\!-\!H$, is a dark-brown powder obtained by gently warming dilute ammonia with mercuric oxid.

Dimercuric Ammonium Oxid, $\begin{smallmatrix}Hg\\Hg\end{smallmatrix}\!\!\diagdown\!\!\diagup N\!-\!O\!-\!N\diagup^{Hg}_{\diagdown Hg}$, is an explosive pale-yellow powder obtained by action of liquid ammonia upon mercuric oxid.

Oxydimercuric Ammonium Iodid, $O<^{Hg}_{Hg}>NH_2\!-\!I$, is a brown solid formed by action of ammonia upon solution of mercuric iodid in an excess of potassium hydroxid. Such a mixture is called *Nessler's solution* and affords a very delicate test for ammonia.

Mercury probably does not form definite compounds with phosphorus and arsenic, but phosphonium and arsonium compounds similar to those of nitrogen have been prepared.

Mercury Salts.—Mercury forms numerous salts. They are prepared by dissolving in acids mercurous oxid or excess of mercury for mercurous salts, and mercuric oxid or carbonate for mercuric salts. The former are less stable and less soluble than the latter and both form with water basic salts.

Mercurous and mercuric chlorates, perchlorates, bromates, iodates, and periodates are all white crystalline solids.

Besides the normal mercurous and mercuric sulfites there are various basic, double, and mixed sulfites.

Mercurous Sulfate, Hg_2SO_4, forms white monoclinic prisms.

Mercuric Sulfate, $HgSO_4$, is a white crystalline insoluble mass which becomes yellow when heated. Heated with water it forms the basic salt, Hg_3SO_4, called *turpeth mineral.* It forms double salts with the alkali sulfates, as $HgSO_4,K_2SO_4,6H_2O$.

Mercurous and mercuric selenites, selenates, chromates, and molybdates are described.

Mercurous Nitrate, $Hg_2(NO_3)_2,2H_2O$, is obtained by dissolving mercury in cold dilute nitric acid. It separates from solution in monoclinic prisms with $2H_2O$. It tends to form basic salts, and in order to keep a solution a little mercury must be placed in the bottom of the bottle. There are also basic, mixed, and double salts.

Mercurous Hydroxynitrate, $Hg<^{O-H}_{NO_3}$, is a yellow crystalline solid.

Mercuric Nitrate, $Hg(NO_3)_2$, is formed when mercury is dissolved in hot nitric acid. On evaporation, crystals of $2Hg(NO_3)_2,H_2O$ separate, and there remains in the solution $Hg(NO_3)_2,2H_2O$. These are converted into basic salts by the action of heat or water.

Mercuric and mercurous phosphates, arsenites, arsenates, antimonates, tantalates, tungstates, and vanadates have been prepared.

Mercurous Carbonate, Hg_2CO_3, is a yellow powder obtained by treating the nitrate with potassium hydrogen carbonate in excess.

Mercuric Carbonates.—Only basic mercuric carbonates are known. Potassium hydrocarbonate precipitates from mercuric nitrate solution the compound $HgCO_3,2HgO$, which may be written thus: $Hg < {}^{O\text{--}Hg\text{--}O}_{O\text{--}Hg\text{--}O} > CO$.

Mercury forms neither borates nor silicates.

CHAPTER XXXVI.

GROUP I A. THE POTASSOIDS. ALKALI METALS.

Lithium 7. Sodium 23. Potassium 39. Rubidium 85.4. Cæsium 133. (Ammonium NH_4.)

History and Occurrence.—The word alkali is from the Arabic and means *the ashes*. The name was originally applied to the solution and salt obtained by leaching the ashes of plants. This was later called *fixed alkali*, to distinguish it from ammonium carbonate, which was called *volatile alkali*.

Potash and soda were first distinguished by Duhamel in 1736. The former was called *vegetable alkali*, because it was supposed to be found only in plants, while the latter took the name *mineral alkali*, from its chief compound, sodium chlorid.

Of the alkali metals sodium is the most abundant, potassium but little less so. Lithium, though widely distributed, is found only in minute quantities, while rubidium and cæsium are quite rare. None of them occur free.

Relations.—The elements of this group are so nearly related that there is no marked chemical differences between them. They are the strongest of all bases, possessing no acidic character at all. The electro positive character increases with the atomic weight and cæsium is positive to all other elements. They present a marked contrast with the halogens, which are extremely negative, and hence the chemical affinity between the elements of the two groups is very strong, and the valence being the same, they unite atom to atom.

As an illustration of the periodic system and the gradation of properties this group is almost ideal. The following may be noted:

As the atomic weight increases—

1. The metallic and basic properties increase.
2. The melting temperatures diminish.
3. The specific gravities increase.

4. The atomic volumes increase.
5. The affinity for oxygen increases.
6. The chemical activity increases.
7. The solubility of the hydroxids and salts increases.

Properties.—These elements are all soft, white metals, which tarnish in the air, lithium slowly, sodium quickly, and potassium instantly, while rubidium and cæsium inflame spontaneously. They all decompose water, lithium slowly, sodium rapidly, potassium with so much vigor as to ignite the escaping hydrogen, and rubidium and cæsium, still more violently. Their flame colors are characteristic, lithium crimson, sodium yellow, potassium violet, and rubidium and cæsium a violet, much like potassium. They all give well-marked spectra by which they may be identified even in the presence of one another, viz., lithium, two lines between the red and yellow; sodium, a double line in the yellow; potassium, two lines, one in the red and one in the violet; rubidium, two lines in the violet, two in the red near the potassium line, and many other lines; cæsium, two in the blue, two in the red, and several in the yellow and green.

Compounds.—The elements of this group are all monads and form similar compounds. They burn to the oxids, which dissolve in water to form caustic alkaline hydroxids. They form halids, sulfids, and hydrosulfids, and with all the acids salts which are soluble, even the silicates. They dissociate in dilute solutions, setting free the univalent elementary ions. Solutions are therefore quite active, though the dry compounds are stable.

Using potassium which may be replaced by either of the other elements, the following are some type compounds:

$$KCl, \ K_2O, \ KHO, \ K_2S, \ KHS, \ K_2SO_4, \ KNO_3, \ K_3PO_4, \ K_2SiO_3.$$
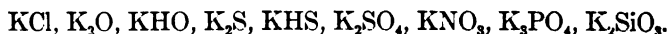
Physical Constants.—Some of the leading physical properties are shown in the following table:

	Atomic Weight.	Specific Gravity.	Atomic Volume.	Melting-point.	Flame Color.
Lithium	7	0.59	11.9	180.0°	Crimson
Sodium	23	0.97	23.6	97.6°	Yellow
Potassium	39	0.87	45.2	62.5°	Violet
Rubidium	85	1.52	56.2	38.5°	Red-violet
Cæsium	133	1.88	70.6	26.0°	Blue-red

LITHIUM.

Symbol Li. Atomic weight 7. Valence I. Specific gravity 0.59. Melting-point 186°.

Occurrence.—Lithium is found in the rare minerals *spodumene*, a lithium aluminum silicate; *petalite*, a lithium sodium aluminum silicate; *lithium mica*, a lithium potassium aluminum silicate; and *triphylite*, a lithium iron manganese phosphate. These minerals may contain from one to five per cent of lithium. Lithium is found widely distributed in very minute quantities in soils, waters, plants, and animals, and·in larger quantities in certain mineral waters (1 to 3 parts to 10,000). It has been observed in the sun and in meteorites.

History.—Lithium was discovered in 1817 by Arfvedson in petalite and spodumene. The metal was first obtained by Bunsen and Matthiessen in 1855. The name is Greek and means *stony*, and the metal was so called because it was then supposed to be found only in rocks and not in the plant and animal bodies.

Preparation.—Lithium is prepared by electrolysis of its chlorid. The chlorid is melted in a porcelain crucible and the electrodes, one carbon and the other iron, introduced. The lithium separates as a bright metallic globule on the negative or iron electrode, from which it is removed to a vessel containing kerosene or benzene.

Physical Properties.—Lithium is a soft white metal, rather malleable and ductile, melts at 180°, and is not volatile at red heat. It is the lightest of solids, its specific gravity being only 0.59.

Chemical Properties.—Lithium tarnishes in the air more slowly than sodium. ignites at 200°, and burns with a brilliant white light. It decomposes water slowly, the heat developed not being sufficient to melt it. It burns when heated in chlorin, bromin, iodin, sulfur, and carbon dioxid. It dissolves in the acids rather easily, in nitric and hydrochloric with great vigor. It attacks glass and porcelain. It may be detected in the minutest quantities by the spectroscope, even to the millionth part of a milligram.

LITHIUM COMPOUNDS.

Lithium yields in solutions only the colorless univalent ion Li·. Its compounds correspond exactly to those of sodium and potassium

Some of the thermal equations are as follows:

(Li,Cl)　　　 = 93,800 c.　(Li,Br)　 = 80,000 c.　(Li,I,Aq.) = 76,100 c.
(Li,H,O,Aq.) = 117,400 c.　(Li,S,O) = 334,200 c.　(Li,N,O) = 111,600 c.
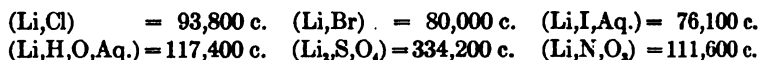
Lithium Halids.—The lithium halids are formed by direct union or by the action of haloid acids upon lithium carbonate. They are all white crystalline solids, and, with the exception of the fluorid, are diliquescent and quite soluble in water. They are LiF, LiCl, LiBr, LiI and LiCN.

Lithium Oxid, Li_2O, is obtained by burning lithium in the air or by igniting the nitrate in a silver vessel. It is a white crystalline solid of specific gravity 2.1. It dissolves slowly in water, easily in acids.

Lithium Hydroxid, LiHO, is obtained by dissolving lithium oxid in water, or by treating lithium carbonate with lime, or lithium sulfate with barium hydroxid. It is a white caustic crystalline solid which melts at red heat and in solution dissociates into the lithium and hydroxyl ions.

Lithium Sulfid, Li_2S, is formed by direct union or by reducing the sulfate with carbon. It dissolves in solution of hydrogen sulfid to form *lithium hydrosulfid,* LiHS.

Lithium Nitrid, Li_xN, is formed when lithium is heated in nitrogen.

Lithium Salts.—Lithium salts are usually obtained by dissolving the carbonate in the acids. They are generally soluble, though the phosphate and carbonate are less so than the corresponding compounds of the other metals of the group. No basic salts are formed.

Lithium Sulfate, Li_2SO_4,H_2O, crystallizes in thin monoclinic plates. The acid salt $LiHSO_4$ and double salt $KLiSO_4$ are formed.

Lithium Alum, $LiAl(SO_4)_2,12H_2O$, is very like potash alum.

Lithium Nitrate, $LiNO_3$, crystallizes in anhydrous rhombic prisms isomorphous with sodium nitrate. Below 10° the hydrated salt $2LiNO_3,5H_2O$ separates.

Lithium Phosphate, Li_3PO_4, is a crystalline powder which differs from the other alkali phosphates by being only slightly soluble. Acid and double salts are formed.

Lithium Carbonate, Li_2CO_3, is a crystalline powder precipitated from lithium chlorid solution by ammonium carbonate. It is only slightly soluble in water, thus differing from the other carbonates of this group and resembling the carbonates of group II. Acid and double carbonates are formed.

Lithium Silicate, Li_2SiO_3, is obtained by fusing lithium carbonate with silicic oxid.

Lithium Fluosilicate, $Li_2SiF_6,2H_2O$, is obtained in monoclinic crystals by action of fluosilicic acid upon lithium carbonate.

SODIUM.

Symbol Na.   Atomic weight 23.   Valence I.   Specific gravity 0.97.
Melting-point 95.6°.

Occurrence.—Sodium compounds are both abundant and widely
distributed, being found in all soils and waters and in the bodies of
plants and animals.   Indeed it is difficult to find anything which
does not contain traces of sodium, as is easily shown by the spectro-
scope or flame reaction.   The most abundant of the compounds is
sodium chlorid, found in saline waters and in beds of rock salt.
Sodium nitrate is found in large deposits in Peru and Bolivia.
Sodium carbonate and sodium sulfate are also found in certain
localities.   Sodium is found in many localities, and sodium chlorid
is an essential constituent of the human body, being found in the
blood and tissues.

History.—Sodium was first separated by Davy in 1807 by
electrolysis of the hydroxid.   Sodium carbonate was called *neter*
by the Hebrews, *nitron* by the Greeks, and *nitrum* by the Romans.
In the fifteenth century this term was applied to saltpeter also, and
to distinguish them the name of the sodium compound was changed
to *natrum* or *natron,* from which word the Latin name of the element,
natrium, is derived.   The English name is from soda (*solida, solid*),
a term applied in the Middle Ages to all alkalis.

Preparation.—Sodium has usually been obtained by reducing
the carbonate with carbon, $Na_2CO_3 + 2C = 3CO + 2Na$.   The ma-
terials are heated in iron cylinders and the sodium vapor condensed
in flat iron receivers and collected under naphtha.

Sodium is now mostly prepared by electrolysis of sodium
hydroxid in iron pots with permeable partitions.   Sodium, liber-
ated at the cathode, floats and is removed from time to time.

Physical Properties.—Sodium is a white metal of specific gravity
0.97, and soft enough to be moulded with the fingers.   At − 20° it is
hard, at 50° it is semifluid, at 95.6° it melts, and at 740° it boils.   Its
vapor density has not been very accurately determined, but it seems
to be below 23, and the molecule is probably monatomic.   By melt-
ing it in a closed tube, allowing it to partially cool and pouring the
liquid away from the solid portion, it may be obtained crystallized in
octahedrons.

Chemical Properties.—Sodium tarnishes quickly and must be kept under a liquid which contains no oxygen, as coal-oil. When heated in the air it burns with a bright-yellow flame. It unites directly with chlorin, bromin, iodin, sulfur, selenium, and tellurium, readily when the materials are moist, with difficulty when dry. It forms alloys with hydrogen, potassium, mercury, and other metals. It decomposes water with liberation of hydrogen, and if the water is warm the hydrogen inflames. It dissolves in ammonia to a blue solution.

Uses.—Sodium is used as a powerful reducing agent, especially in the preparation of silicon, boron, magnesium, and aluminum, and as amalgam in separating gold from quartz.

SODIUM COMPOUNDS.

Sodium is univalent in all its compounds and its solutions contain the colorless elemental ion $Na^{.}$. This ion is very active, uniting readily with nearly all negative ions, but not easily separating as th·metal. The sodium compounds are very numerous, nearly every one theoretically possible being realized. The metal is strongly basic and shows no acid properties. Its compounds are generally exothermic, but many of its salts dissolve in water with absorption of heat.

Some of the more important thermal equations are as follows:

(Na_2,O)	= 80,400 cal.	(Na,H,O)	= 101,900 cal.
(Na_2,S)	= 87,000 cal.	(Na,Cl)	= 97,600 cal.
(Na,Br)	= 85,800 cal.	(Na,I)	= 69,100 cal.
(Na,Cl,O_3)	= 86,800 cal.	(Na,N,O_3)	= 111,300 cal.
(Na_2,H,P,O_4)	= 410,900 cal.	(Na_2,S,O_3)	= 268,500 cal.
(Na_2,S,O_4)	= 328,800 cal.	(Na,H,S,O_4)	= 267,800 cal.
(Na_2,C,O_3)	= 272,600 cal.	(Na,H,C,O_3)	= 229,900 cal.
$(Na_2,S_2,O_3,5Aq)$	= 265,200 cal.		

The heat of solution of some of the compounds is as follows:

NaHO =	9,900 cal.	Na_2O =	55,000 cal.	NaCl	= −1.200 cal.
Na_2SO_3 =	−11,000 cal.	$NaNO_3$ =	−5,000 cal.	$NaHCO_3$ =	−4,300 cal.
		Na_2CO_3 =	5,600 cal.		

Sodium Hydrid, NaH.—Fused sodium between 300° and 400° absorbs about 237 volumes of hydrogen, forming an alloy whose

composition is approximately NaH. It forms white, silky needles which are instantly decomposed by water and acids.

Sodium Halids.—Sodium has strong affinity for the halogens, forming with them the typical haloid or binary salts. Sodium chlorid is the one which gives them the name *halogens, salt-makers.* They are all colorless, stable, anhydrous solids which crystallize in cubes and have a salty taste. They also form at low temperatures crystalline hydrates. There are many double halids or halo salts, of which native cryolite, $3NaF,AlFl$ or Na_3AlF_6, is an example.

Sodium Fluorid, NaF, may be prepared by dissolving the proper amount of the hydroxid or carbonate in hydrofluoric acid, evaporating in a platinum dish, and gently igniting. It crystallizes in cubes and octahedrons, is slightly soluble in water (4 pts. to 100), and is insoluble in alcohol.

Sodium Hydrogen Fluorid, NaF,HF, or Na—F=F—H, is obtained in octadehral crystals of sharp taste by evaporating a solution of sodium fluorid in hydrofluoric acid.

Sodium Chlorid, NaCl.—This is the most abundant and most important compound of sodium and deserves a somewhat detailed description.

Occurrence.—Sodium chlorid or common salt occurs in large quantities in sea and saline waters and in the mineral *halite* or rock-salt. Extensive beds of the latter are found in New York, Michigan, Virginia, and Louisiana. It is also found in varying quantities in all fresh waters. In mountainous and sandy regions the water may contain even less than one part in 100,000, while in the Great Salt Lake it reaches 20 per cent and in the Dead Sea 22 per cent. The waters of the Mediterranean Sea contain 3.8 per cent and those of the Atlantic Ocean 3.6 per cent, while those of the Baltic Sea contain but 5 parts in 1000. It is found in all soils and many plants, and is an important food of all animals, being an essential constituent of blood and tissues.

Preparation.—Sodium chlorid may be prepared by direct union or by the action of sodium hydroxid upon hydrochloric acid:

$$NaHO + HCl = H_2O + NaCl.$$
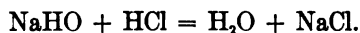
The commercial article is always obtained from nature, the three principal sources being sea-water, salt springs and wells, and rock-salt.

Salt is obtained from sea-water in warm climates, especially along the coast of the Mediterranean Sea, by a simple process. The water at high tide is allowed to flow into shallow basins called *salterns* or *salt gardens*, where it evaporates in the sun, a new supply being added each day. The first product is nearly pure sodium chlorid, but later a mixture of sodium chlorid and magnesium chlorid is obtained. The residual liquid contains a number of other salts, especially bromids, and is used as a source of bromin compounds.

Most of the salt manufactured in the United States comes from salt springs and wells. The brine is concentrated by exposure to the air and finally evaporated in shallow iron pans. The air evaporation is usually hastened by allowing the water to flow through stacks of loose brushwood called *graduators*, whereby it is soon so concentrated as to contain 20 per cent of salt.

Rock-salt is mined in various ways. It may be brought to the surface and used as such when it is sufficiently pure. It is more generally dissolved and recrystallized. It may be dissolved by admitting water to the mine and then pumping the water out when it is saturated with the salt.

Physical Properties—Sodium chlorid crystallizes in white lustrous cubes and hopper-shaped masses of specific gravity 2.13. It has a pleasant, salty taste and is soft enough to be easily cut with a knife. It is coarse or fine according to the rapidity of the evaporaation. It melts at 772°, and is volatile a little above this. It dissolves in water with absorption of heat ($NaCl,Aq. = -1200$ cal.), the solubility increasing slightly as the temperature rises. One hundred parts dissolve at 0° 35.5 parts, at 14° 35.8, at 50° 36.98, and at 100° 39.6. The specific gravity increases regularly with the quantity of the salt dissolved, and a specific-gravity table may be used to determine the strength of solutions. A 10 per cent solution has a specific gravity 1.14. Its addition to water raises the boiling-point and lowers the freezing-point. A 30 per cent solution boils at 109° and freezes at − 21°. By cooling the saturated solution several hydrates are obtained: at 10°, $NaCl,2H_2O$, and at − 22°, $NaCl,10H_2O$. It is precipitated from solution by hydrochloric acid, and thus may be separated from the other salts with which it may be mixed. Common salt is slightly deliquescent because of the presence of a little magnesium chlorid as an impurity.

Chemical Properties.—Sodium chlorid is stable, but in solution is chemically quite active because of the free ions Na· and Cl′. It is decomposed by most acids except hydrochloric, with liberation of

hydrogen chlorid. It dissociates strongly in solution; decinormal 84 per cent, centinormal 93.5 per cent, millinormal 98 per cent.

Uses.—Sodium chlorid is an important food, being essential to animal life. It is an antiseptic and preservative for meats, butter, and other foods. It is largely used in the manufacture of chlorin and alkalis and other salts of sodium, and in glazing earthenware.

Sodium Bromid, NaBr, is prepared by direct union of the elements or by action of hydrogen bromid upon sodium hydroxid. It forms white cubes of sharp salty taste and specific gravity 3. It melts at 708°. It is more soluble than the chlorid, and the solubility increases more rapidly as the temperature rises, 100 parts of water dissolving 88 at 20° and 114 at 100°. The saturated solution boils at 121°. Above 30° it crystallizes anhydrous, below as $NaBr,2H_2O$.

Sodium Iodid, NaI, is formed by direct union of the elements, or by neutralizing hydriodic acid with sodium carbonate, or by action of iodin and hydrogen iodid upon sodium hydroxid. It crystallizes from solution above 40° anhydrous, below 40° as $NaI,2H_2O$. It is deliquescent and melts at 628°. It is more soluble than the bromid or chlorid, 100 parts of water dissolving 158 parts at 0°, 178 at 20°, and 312 at 100°. The saturated solution boils at 141°.

Sodium Cyanid, NaCN, is prepared by action of hydrocyanic acid upon sodium hydroxid. It is a white deliquescent solid which crystallizes with difficulty and forms two hydrates, $2NaCN,H_2O$ and $NaCN,2H_2O$.

Sodium Oxid, Na_2O, is formed, together with the peroxid, when sodium burns in moist air. It is better prepared by heating sodium with sodium hydroxid. It is a gray amorphous solid of specific gravity 2.8. It melts at red heat and volatilizes at a higher temperature. It unites vigorously to water to form the hydroxid.

Sodium Peroxid, Na_2O_2, is formed when sodium burns in an excess of dry air or oxygen. It deliquesces slowly in the air and absorbs carbon dioxid, becoming sodium carbonate. When dissolved rapidly in water oxygen is evolved, but if added slowly hydrogen peroxid is obtained. By evaporating the solution over sulfuric acid crystals of $Na_2O_2,8H_2O$ are obtained.

Sodium peroxid is used as an oxidizing agent in analytic operations and in bleaching.

Sodium Hydroxid, NaHO.—Pure sodium hydroxid is best obtained by action of sodium or sodium oxid upon water. Commercially it is prepared on a large scale by action of slaked lime upon sodium carbonate: $CaH_2O_2 + Na_2CO_3 = CaCO_3 + 2NaHO$, or by the electrolysis of sodium chlorid in the presence of water.

Sodium hydroxid, popularly known as *caustic soda*, is a white,

brittle, opaque, fibrous solid which is strongly caustic and highly deliquescent, melts below red heat, and volatilizes at white heat. It dissolves in water in all proportions, evolving much heat, and if the solution be evaporated at low temperatures, various hydrates are formed.   At $-8°$ crystals of $NaHO,7H_2O$ separate.   The solutions boil at elevated temperatures, 36 per cent at 130° and 83 per cent at 260°.   The specific gravity of the solution indicates the per cent of the hydroxid: 1 per cent 1.01, 10 per cent 1.12, 20 per cent 1.23, and 50 per cent 1.54.   Its dissociation into $Na^{.}$ and HO' is, decinormal 90 per cent, centinormal 99.5 per cent, five hundredth normal 100 per cent.

Sodium hydroxid is used in many industrial operations, notably in the manufacture of soap and paper, and in the purification of carbolic acid and petroleum residues.

Sodium Sulfid, Na_2S, is obtained by passing hydrogen sulfid over dry sodium hydroxid or by reducing the sulfate with carbon or hydrogen. It is an amorphous, deliquescent, flesh-colored solid.   It dissolves readily in water, but the solution is unstable and soon contains polysulfids, sulfates, and thiosulfates.   It forms several hydrates, the one, $Na_2S,9H_2O$, being most easily separated.

Sodium Disulfid, Na_2S_2, and polysulfids are formed in sodium sulfid solutions.

Sodium Hydrosulfid, NaHS, is obtained by treating sodium sulfid solution with hydrogen sulfid and evaporating in an atmosphere of hydrogen sulfid.

Sodium Selenid, Na_2Se; **Diselenid,** Na_2Se_2; **Tellurid,** Na_2Te; **Ditellurid,** Na_2Te_2; **Nitrid,** Na_3N; **Phosphid,** Na_3P, and **Arsenid,** Na_3As, have been prepared.

Sodium Fluosilicate, Na_2SiF_6, falls as a gelatinous precipitate when fluosilicic acid is added to sodium chlorid solution.

Sodium Salts.—Sodium is strongly basic, yields an ion which is very active, and forms salts with all the acids.   These are generally soluble in water, colorless and crystalline, and many are deliquescent.

Sodium Chlorate, $NaClO_3$, is obtained by dissolving sodium carbonate in chloric acid or by the action of sodium silicofluorid upon potassium chlorate.   It crystallizes in tetrahedrons and resembles potassium chlorate in properties, though it is much more soluble in water, 100 parts of water dissolving 99 parts at 20° and 232 at 100°.   It is used in the manufacture of anilin black.

Other salts of the halogen acids are:
Sodium hypochlorite, NaClO, a bleaching and oxidizing agent.

Sodium perchlorate, $NaClO_4$, a very soluble crystalline salt
Sodium hypobromite, $NaBrO$, only in unstable solution.
Sodium bromate, $NaBrO_3$, crystalline salt isomorphous with $KBrO_3$.
Sodium iodate, $NaIO_3$, crystalline solid.
Sodium periodates, $Na_2H_3IO_6$ and $Na_3H_2IO_6$ and $NaIO_4$, crystalline salts.

Sodium Hyposulfite, $NaHSO_2$, is formed by the action of zinc upon sodium hydrogen sulfite. The solution is treated with lime, whereby zinc oxid and calcium sulfite are precipitated. By treating the clear liquid with alcohol the sodium hyposulfite is thrown down in fine needle-shaped crystals which are dried in vacuo and must be kept away from the air. It is used by the dyer for reducing indigo and in the laboratory for determining free or loosely combined oxygen.

Sodium Sulfite, $Na_2SO_3,7H_2O$, is obtained by action of sulfurous oxid upon sodium carbonate in excess. It becomes anhydrous when heated and its solution is alkaline by hydrolysis.

Sodium Hydrogen Sulfite, $NaHSO_3$, is obtained by saturating a solution of sodium carbonate with sulfurous oxid in the cold.

Sodium Sulfate, Na_2SO_4, occurs native as *thenardite*. It is produced in many chemical operations, generally from sodium chlorid, as by action of hot sulfuric acid, magnesium sulfate, or sulfurous oxid and oxygen (known as the Hargreaves process):

$$2NaCl + MgSO_4 = MgCl_2 + Na_2SO_4.$$
$$2NaCl + SO_2 + O + H_2O = 2HCl + Na_2SO_4.$$
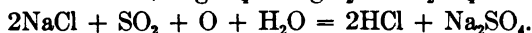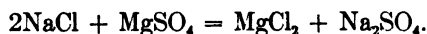
It is also a by-product of the manufacture of nitric acid from sodium nitrate.

The anhydrous salt is known as salt cake and is used in large quantities in the soda and alkali industries, and in the manufacture of glass.

Sodium sulfate forms three distinct hydrates, viz., with 1, 7, and 10 molecules of water. The last, $Na_2SO_4,10H_2O$, is most easily obtained and is known as *Glauber's salt*, Glauber having described it in 1568. It crystallizes in monoclinic prisms, has a bitter taste, is efflorescent, and looses its water when heated. The three hydrates exhibit different degrees of solubility, and this explains the peculiar action of Glauber's salt with water. It dissolves in 100 parts of water 12 parts at 0°, 48 parts at 18°, 100 parts at 25°, 200 parts at

30°, 327 parts at 33°. On further increase of temperature the solubility falls, being 263 parts at 50° and 238 parts at 100°. This phenomenon is explained on the supposition that above 33° the hydrate dissociates and that it is the anhydrous or monohydrated salt that is dissolving.

Sodium sulfate furnishes the best example of supersaturation. If the solution saturated at 33° be allowed to cool the salt remains in solution. If a crystal of the salt be added the liquid becomes at once a solid crystalline mass.

Glauber's salt is used in medicines as a purgative.

Sodium Hydrogen Sulfate, $NaHSO_4$, is prepared by action of sulfuric acid upon sodium chlorid or sodium sulfate. It crystallizes from solution in large triclinic prisms.

Sodium Alum, $NaAl(SO_4)_2,12H_2O$, is the most soluble of all the alums.

Sodium Disulfate, $Na_2S_2O_7$, is obtained by heating a mixture of sulfuric oxid and sodium chlorid: $2NaCl + 3SO_3 = SO_2Cl_2 + Na_2S_2O_7$, or by gently igniting sodium hydrogen sulfate.

Sodium Thiosulfate, $Na_2S_2O_3,5H_2O$, is known as *hyposulfite of soda,* or simply *hypo.* It is largely used in photography as a fixing solution to remove the unchanged silver chlorid from the plate, and as an antichlor in the paper manufacture, and in other bleaching processes. It is prepared by boiling sodium sulfite solution with sulfur.

Sodium thiosulfate forms large monoclinic prisms which are deliquescent and easily soluble in water. It melts in its water of crystallization at 56°, loses the water at 100°, and decomposes on further heating into Na_2SO_4 and Na_2S_5. It is unstable, being readily decomposed by the acids and the halogens.

Sodium forms selenites, selenates, tellurites, tellurates, also chromates, molybdates, and tungstates.

Sodium Nitrite, $NaNO_2$, is obtained by reducing sodium nitrate with lead, iron, or graphite. It is a very soluble, slightly alkaline, and unstable deliquescent crystalline solid. It is largely used, instead of the more costly potassium nitrite, in the dye industry, and in preparation of azo compounds.

Sodium Nitrate, $NaNO_3$, is known as *Chili saltpeter* or *soda niter.* It occurs in large deposits in the rainless regions of Peru and Bolivia, associated with common salt, gypsum, and sodium sulfate. The

crude salt.is purified by recrystallization. It is artificially prepared by dissolving sodium hydroxid in nitric acid. It is quite soluble in water, 100 parts dissolving 87 parts at 20°, 100 parts at 40°, and 180 parts at 100°. It crystallizes in obtuse rhombohedrons approximating cubes, and hence is called *cubic saltpeter.* It melts at 310° and decomposes at a higher temperature. It is deliquescent, and cannot be used for gunpowder. Its chief use is in the manufacture of nitric acid and potassium nitrate.

Phosphates.—Sodium forms salts with all the acids of phosphorus. They all crystallize well, with more or less water of crystallization. The orthophosphates give with silver nitrate yellow precipitates of silver phosphate, Ag_3PO_4.

Sodium Phosphate, Na_3PO_4, $12H_2O$.—The normal sodium phosphate occurs in the bones of animals and in native phosphates. It may be prepared by evaporating a solution in molecular proportions of disodium phosphate and sodium hydroxid, $Na_2HPO_4 + NaHO = H_2O + Na_3PO_4$. It crystallizes in hexagonal prisms with twelve molecules of water. Its solution is strongly alkaline because of hydrolysis, $Na_3PO_4 + H_2O = Na_2HPO_4 + Na^{\cdot}, HO'$.

Disodium Phosphate, $Na_2HPO_4, 12H_2O$, is the common sodium phosphate of commerce. It is prepared by neutralizing phosphoric acid with sodium hydroxid or carbonate, or by the action of sulfuric acid upon the trisodium phosphate found in bones and native phosphates (see Phosphorus). It forms monoclinic prisms of specific gravity 1.5. It effloresces, melts at 35° in its water of crystallization, and at 45° gradually looses the whole of the water. Its solubility increases as the temperature rises, 100 parts dissolving 2.5 parts at 0°, 9 parts at 20°, 82 parts at 50°, and 99 parts at 100°. It has a cooling, saline taste and alkaline reaction.

Sodium phosphate is much used in medicine as a mild purgative and in the laboratory as a reagent, especially in the determination of magnesium.

Monosodium Phosphate, NaH_2PO_4, H_2O, is obtained by adding phosphoric acid to disodium phosphate until barium chlorid gives no precipitate, $Na_2HPO_4 + H_3PO_4 = 2NaH_2PO_4$. It crystallizes with one molecule of water in efflorescent monoclinic prisms. Its solution is acid by hydrolytic dissociation, $NaH_2PO_4 + H_2O = Na_2HPO_4 + H^{\cdot}, H^{\cdot}, H^{\cdot}, PO_4'''$.

Sodium Metaphosphate, $NaPO_3$, is an amorphous glass-like substance obtained by heating monosodium phosphate or sodium

ammonium phosphate. It may also be obtained in crystals with one and a half molecules of water.

Sodium Diphosphate, $Na_4P_2O_7$, $10H_2O$, is prepared by heating disodium phosphate, $2Na_2HPO_4 = H_2O + Na_4P_2O_7$. It crystallizes with ten molecules of water.

Sodium Ammonium Phosphate, $NH_4NaHPO_4,4H_2O$, known as *microcosmic salt,* crystallizes from a mixed solution of disodium phosphate and ammonium chlorid, $Na_2HPO_4 + NH_4Cl = NH_4NaHPO_4 + NaCl$. When heated it yields sodium metaphosphate. It is used in blowpipe analysis to form on platinum wire a bead of sodium metaphosphate which dissolves metallic oxids, assuming characteristic colors.

Sodium Arsenates.—The sodium arsenates are exactly analogous to the phosphates. An impure arsenate is prepared by boiling a mixture of arsenous oxid, sodium hydroxid, and sodium nitrate. It is used in calico-printing for cleaning the cloth after mordanting.

Other salts of sodium belonging in this connection are the arsenites, thioarsenites, thioarsenates, antimonates, thioantimonates (Schlippe's salt), vanadates, metavanadates, fluovanadates, tantalates, and fluotantalate.

Sodium Carbonate.—This important compound occurs native as *natron,* $Na_2CO_3,10H_2O$, and as *thermonatrite,* Na_2CO_3,H_2O. It is found in the ashes of sea-plants, and this was the chief source of supply until 1793, when its manufacture from sodium chlorid was begun.

The anhydrous salt is a white porous alkaline solid known as *soda ash.* It has specific gravity 2.5, melts at 850°, dissolves in water with evolution of heat, crystallizes from solution in monoclinic prisms of composition $Na_2CO_3,10H_2O$, and specific gravity 1.45. This is known as *washing-soda.* It is efflorescent and looses all its water but one molecule at 34°, and parts with this at 100°. Several other hydrates can be formed. As in the case of sodium sulfate, so also with this compound there is an irregularity in its solubility. One hundred parts of water dissolve at 0° 7 parts, at 32° 59 parts, at 79° 46.2 parts, and at 100° 45.4 parts.

The commercial sodium carbonate always contains as impurities the chlorid, sulfate, and hydroxid of sodium. It is used in the manufacture of soap and glass and in the preparation of nearly all the other sodium compounds.

Sodium Hydrocarbonate, $NaHCO_3$, is known as *bicarbonate of soda* or *cooking soda.* It is a white alkaline powder consisting of small monoclinic crystals. It is prepared by the action of carbon dioxid upon sodium carbonate: $Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$. It is less soluble than the normal salt and the solubility increases as the temperature rises. One hundred parts of water dissolve at 0° 8 parts, at 20° 9.8 parts, at 50° 12.7 parts, at 70° 14.6 parts. By heating the salt or boiling the solution it is converted into the normal carbonate. If the solution be 'boiled and cooled, monoclinic crystals of the so-called sesquicarbonate $Na_2CO_3,2NaHCO_3,2H_2O$ separate. This compound occurs native in Hungary and Egypt and in the Rocky Mountains as the mineral *trona.*

Sodium hydrocarbonate is largely used in bread-making, in baking-powders, and in effervescing-powders.

The sodium carbonates are alkaline by hydrolytic dissociation,

$$Na_2CO_3 + H_2O = Na\cdot,HO' + Na\cdot,HCO_3'$$
$$NaHCO_3 + H_2O = Na\cdot,HO' + H_2O + CO_2.$$
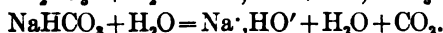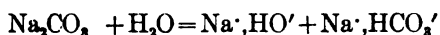
The Alkali Industry.—Since sodium carbonate is of such commercial importance its manufacture is of interest. There are two general methods, known respectively as the Le Blanc process and the Salvay or ammonia-soda process. The first was devised by the Frenchman Le Blanc in 1794. The second was introduced as early as 1838, but was first made available by Salvay in 1861, in a factory near Brussels.

Le Blanc process.—This process consists of three parts:

1. Preparation of the salt cake Na_2SO_4 by the action of sulfuric acid upon common salt. There are two stages in the action represented by the equations

$$NaCl + H_2SO_4 = HCl + NaHSO_4; \quad NaCl + NaHSO_4 = HCl + Na_2SO_4.$$
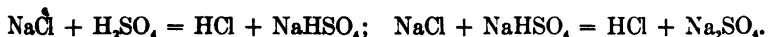
2. The conversion of the salt cake into black ash, or of the sodium sulfate into sodium carbonate, by means of calcium carbonate and carbon:

$$NaSO_4 + CaCO_3 + 2C = CaS + 2CO_2 + Na_2CO_3.$$
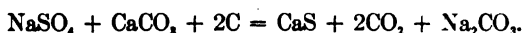
3. The separation of the sodium carbonate by lixiviation of the black ash and evaporation of the solution.

The Salvay process. — The Salvay or ammonia-soda process is based upon the decomposition of sodium chlorid by carbon dioxid and ammonia:

$$NH_4OH + CO_2 + NaCl_3 = NH_4Cl + NaHCO_3.$$

The slightly soluble sodium hydrogen carbonate is precipitated and the liquid is filtered or drained away. The ammonia is recovered by treating the liquid with lime or magnesia and is used over and over.

Soda from cryolite.—Sodium carbonate is also manufactured from

cryolite by heating it with chalk:

$$Na_3AlF_6 + 3CaCO_3 = 3CaF_2 + 3CO_2 + Na_3AlO_3.$$

The sodium aluminate is dissolved out with water and decomposed with carbon dioxid:

$$2Na_3AlO_3 + 3CO_2 + 3 H_2 + O = 2H_3AlO_3, 3Na_2CO_3.$$
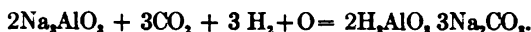
Manufacture of sodium hydrogen carbonate, $NaHCO_3$.—This salt is prepared by exposing the crystalline carbonate to the action of carbon dioxid in large chambers: $Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$.

Manufacture of sodium hydroxid, NaHO.—Sodium hydroxid is made by heating the solution of the carbonate with milk of lime or by the electrolysis of sodium chlorid.

Sodium Metasilicate, Na_2SiO_3, is formed when molecular proportions of silicic oxid and sodium carbonate are fused together.

Sodium Trisilicate, $Na_6Si_3O_{10}$, is formed when silicic oxid is fused with sodium carbonate in excess.

Sodium Tetrasilicate, $Na_2Si_4O_9$, commonly known as silicate of soda or *soluble glass,* is obtained by heating together sand, soda ash, and charcoal. It is a colorless glassy mass, which dissolves in water to a viscid liquid. It is used in fixing fresco colors, in making artificial stone, as a cement for glass, and as a constituent of soap.

Sodium Fluosilicate, Na_2SiF_6, is obtained by action of fluosilicic acid upon a sodium salt. It is a white powder scarcely soluble in water.

Sodium Stannate, Na_2SnO_3, is prepared by dissolving stannic acid in sodium hydroxid. It crystallizes with varying quantities of water, most easily with 3, 8, or 9 molecules.

Normal Sodium Borate, Na_3BO_3, is obtained by fusing boric oxid with sodium hydroxid. It is unstable and is changed by water into a hydrated metaborate.

Sodium Metaborate, $NaBO_2, 4H_2O$, is formed when borax is fused with sodium carbonate.

Sodium Tetraborate, $Na_2B_4O_7, 10H_2O$, is known as *borax,* and is the most important compound of boron. It is found native in Thibet, Peru, Ceylon, and California as the mineral *tincal.* Borax Lake, California, contains one pound of borax to thirteen gallons of water. It may be prepared by neutralizing boric acid with sodium carbonate:

$$H_3BO_3 + Na_2CO_3 = CO_2 + 6H_2O + Na_2B_4O_7$$

Borax crystallizes in large monoclinic prisms of specific gravity 1.71. If the temperature be kept during evaporation between 70°

and 80° it crystallizes as $Na_2B_4O_7,5H_2O$ in octahedrons. This is called octahedral borax. Both salts swell when heated, loose water, and become a porous mass, and finally melt to a transparent glass which in fusion dissolves many metallic oxids with characteristic colors. This is called the *borax bead* and is much used in qualitative and blowpipe analysis.

Because of its property of dissolving metallic oxids borax is used as a flux in working silver and gold, and in soldering and welding. It is used in the manufacture of porcelain and in glass-painting, as an antiseptic, and as a constituent of scalp-cleansing mixtures.

The formula of borax may be written

$$Na-O-B-O-B = O \qquad Na-O-B<^O_O>B$$
$$\qquad\qquad >O \qquad or$$
$$Na-O-B-O-B = O \qquad Na-O-B<^O_O>B$$
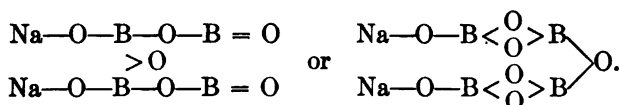
Sodium Aluminates.—Several sodium aluminates can be prepared. See "Soda from cryolite," above.

Sodium Acetate, $NaC_2H_3O_2,3H_2O$.—Sodium forms salts with nearly all the organic acids. The most important of these is sodium acetate, a white crystalline solid which melts in its water of crystallization at 58°. Its usefulness in analytic operations depends upon the fact that it removes from acid solutions the hydrogen ion forming the sodium salt of the acid and leaving the solution acid with the undissociated acetic acid.

POTASSIUM.

Symbol K. Atomic weight 39. Valence I. Specific gravity 0.87. Melting-point 62.5°.

Occurrence.—The principal native compounds of potassium are *sylvite*, KCl, *niter*, KNO_3, *carnallite*, $KCl,MgCl_2,6H_2O$, *kainite*, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, and the various silicates of which potassium is a constituent, as *orthoclase*, *leucite*, *mica*, *biotite*, etc. It occurs very widely distributed in rather small quantities in nearly all rocks and soils, in sea, salt, and mineral waters, and is an essential food of both plants and animals.

History.—The compounds of potassium have been known and used from the earliest times. The metal was first prepared by Davy in 1807 by electrolysis of the hydroxid, and was named by him after the word *potash*, a term long applied to the substance obtained from ashes by leaching and evaporation.

Preparation.—Potassium may be prepared—

1. By electrolysis of the fused hydroxid (method of Davy).
2. By reduction of the hydroxid with iron (method of Gay-Lussac and Thénard).
3. By reducing the carbonate with carbon (method of Brunner):

$$K_2CO_3 + 2C = 3CO + K_2.$$
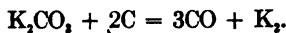
The mixture is strongly heated in iron cylinders and the potassium vapor conducted into iron condensers. The potassium has a tendency to unite to the carbon monoxid to form a very explosive compound, and to prevent this the condensers are made flat so as to cool the vapor rapidly. On a small scale the mixture of potassium carbonate and carbon may be obtained by heating cream of tartar, potassium hydrogen tartrate, $KHC_4H_4O_6$:

$$2KHC_4H_4O_6 = K_2CO_3 + 3C + 5H_2O + 4CO.$$
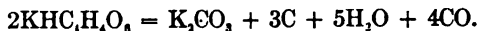
Illustrations.—The separation of potassium by electrolysis may be shown as follows: Melt some potassium hydroxid in a platinum dish connected with the positive pole of a powerful battery and use as the negative electrode a stout platinum wire flattened at the end and made into a sort of spoon. On bringing this into the fused potash oxygen and hydrogen are rapidly evolved and globules of potassium collect on the wire.

The preparation of potassium by reduction of the carbonate may be shown by heating a mixture of the carbonate and magnesium powder in a porcelain boat enclosed in a combustion-tube, through which passes a stream of hydrogen. The potassium forms a metallic mirror in the tube.

Physical Properties.—Potassium is a lustrous white metal of specific gravity 0.87. It is soft enough to be moulded with the fingers and welds like hot iron when two bright surfaces are pressed together. At 0° it is hard and brittle, at 62.5° it melts, and at 720° it boils, yielding a green vapor. The vapor density has not been accurately determined, but is such as to indicate that the molecule is monatomic. It may be obtained in octahedral crystals by melting it in a tube filled with coal-gas or hydrogen and as it cools pouring the liquid away from the solidified portion. It dissolves in liquid ammonia to a deep-blue solution. Its spectrum contains two characteristic bright lines, one in the red and the other in the violet. These serve for the detection of the merest trace of potassium.

Chemical Properties.—Potassium is the most electro-positive and the most active of all the metals except rubidium and cæsium. It tarnishes immediately in moist air, becoming covered first with the oxid and then the carbonate, but is not readily attacked by dry oxygen. When heated it burns vividly in air or oxygen with violet flame. It burns also in carbon dioxid, chlorin, nitrogen dioxid, and vapors of bromin, iodin, and sulfur. It decomposes water with such violence that the hydrogen is inflamed at once. It swims on the surface of the water, becoming finally a melted globule of potassium hydroxid which explodes when it is sufficiently cool to come in actual contact with the water, because of the sudden formation of a large amount of steam.

Potassium is a powerful reducing agent and is used in separation of such elements as boron, silicon, magnesium, and aluminum. Sodium has the same property and is more used because it is cheaper and more manageable.

Illustration.—The color of potassium vapor may be shown by heating a fragment of the metal in a tube through which a stream of hydrogen is passing, and the color of the flame is shown by igniting the escaping gases.

Potassium Alloys.—Potassium forms alloys most readily with the alkali metals and mercury.

Potassium-sodium alloy is formed when the metals are melted together under petroleum. It is a liquid which resembles mercury and is used in thermometers which are intended to register high temperatures.

Potassium amalgam is a powerful reducing agent, but is not much used, as sodium amalgam is cheaper and just as efficient.

POTASSIUM COMPOUNDS.

Potassium is univalent in all its well-defined compounds, and its solutions contain the very active colorless elemental ion $K^{.}$, which is not easily separated as the metal. Like sodium it forms nearly all the theoretical compounds. It is still more strongly basic than sodium and is entirely destitute of acid properties. With the exception of rubidium and cæsium it makes the strongest and most caustic alkali. Its compounds are highly exothermic, but their heat of solution is generally negative.

Thermal equations are as follows:

(K,Cl)	= 104,300 c.	(K,Br)	= 95,100 c.	(K,I)	= 80,100 c.
(K,H,O)	= 103,200 c.	(K$_2$,S)	= 101,200 c.	(K,H,S)	= 58,500 c.
(K,Cl,O$_4$)	= 95,900 c.	(K,Br,O$_3$)	= 84,100 c.	(K,I,O$_3$)	= 124,500 c.
(K$_2$,S,O$_4$)	= 273,800 c.	(K$_2$,S,O$_4$)	= 344,600 c.	(K,H,S,O$_4$)	= 277,500 c.
(K,N,O$_3$)	= 119,500 c.	(K$_2$,C,O$_3$)	= 281,100 c.	(K,H,C,O$_3$)	= 235,600 c.

Some heats of solution are as follows:

KHO	= 13,300 c.	K$_2$S	= 10,000 c.	KHS	= 600 c.
KCl	= − 4,400 c.	KBr	= −5,100 c.	KI	= −5,100 c.
KClO$_4$	= − 12,500 c.	KBrO$_3$	= −9,800 c.	KIO$_3$	= −6,800 c.
K$_2$SO$_4$	= − 6,400 c.	K$_2$S$_2$O$_7$	= 11,200 c.	KHSO$_4$	= −3,800 c.
KNO$_3$	= − 8,500 c.	K$_2$CO$_3$	= 6,500 c.	KHCO$_3$	= −5,300 c.

Potassium Hydrid, KH.—When hydrogen is passed over potassium heated to 360° a metallic, shining, brittle alloy is obtained which has the composition KH. It takes fire spontaneously in the air, and reacts violently with water, forming potassium hydroxid and hydrogen.

Potassium Halids.—Potassium, like sodium, forms typical halids. Potassium chlorid is the only one which occurs native in considerable quantity. They may all be prepared by neutralizing the haloid acids with potassium carbonate or hydroxid. The bromid and iodid are more advantageously obtained by other methods. They are all highly ionized in solution.

The potassium halids are all white soluble salts which crystallize in cubes. They are usually anhydrous, but hydrous forms may be obtained by crystallizing at low temperatures. They are all decomposed by sulfuric acid, yielding the haloid acid

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl.$$
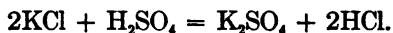
They form many double salts of which the fluorids seem to be the most common. These may be regarded as close compounds if we make the valence of the halogen three. Examples are HF,KF = H—F = F—K;

$$FKBF_3 = K—F = F—B{\Big\langle}{}^{F}_{F}\|;\ 2KF,SiF_4 = {{K—F=F}\atop{K—F=F}}{\Big\rangle}Si{\Big\langle}{}^{F}_{F}\|.$$
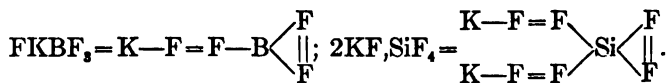
Illustration.—To show the action of sulfuric acid upon the halids put in separate test-tubes sodium chlorid, potassium bromid, and potassium iodid, and add a little strong sulfuric acid. The first tube yields

only hydrogen chlorid, the second hydrogen bromid with some bromin, the third hydrogen iodid with much iodin. This is because of the smaller affinity of hydrogen for bromin and iodin.

Potassium Fluorid, KF, is deliquescent and has a sharp taste. It unites with hydrogen fluorid to form H—F÷F—K.

Potassium Chlorid, KCl.—The chief sources of potassium chlorid are the minerals *sylvite,* KCl, and *carnallite,* $KCl,MgCl_2,6H_2O$. When the latter substance is dissolved in water the double salts dissociates and on evaporation the less soluble KCl crystallizes out first.

Potassium chlorid crystallizes in cubes of specific gravity 1.9. It melts at 730° and is volatile at red heat. It has a cooling, saline taste, sharper than that of sodium chlorid. One hundred parts of water dissolve 28 parts at 0° and 57 parts at 100°. As the cheapest salt of potassium it is the starting-point for the formation of other potassium compounds.

Potassium Bromid, KBr, is prepared by treating potassium hydroxid with bromin: $6KHO + 6Br = 5KBr + KBrO_3 + 3H_2O$. The bromid and bromate may be separated by crystallization, or the bromate may be reduced by heating the mixture with charcoal:

$$KBrO_3 + 3C = 3CO + KBr.$$
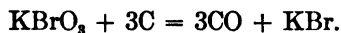
Potassium bromid has a sharp, saline taste, and forms white cubes of specific gravity 2.4. One hundred parts water dissolve 53 parts at 0°, 65 at 20°, 75 at 40°, and 102 at 100°. It is much used in medicine, chiefly as a sedative.

Potassium Iodid, KI, is prepared in the same manner as the bromid, or by mixing iron filings and iodin under water and adding potassium carbonate. The ferrous ferric iodid formed at first is decomposed by the carbonate

$$Fe_3I_8 + 4K_2CO_3 + 4H_2O = Fe_3(HO)_8 + 4CO_2 + 8KI.$$
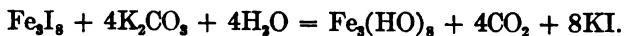
The ferrous ferric hydroxid precipitates, the carbon dioxid escapes, and the potassium iodid remains in the solution from which it is separated by evaporation.

Potassium iodid forms white cubes of sharp taste and specific gravity 2.9. It melts at 634° and is volatile at a temperature a little higher. One hundred parts of water dissolve 128 parts at 0°, 140 at 10°, 152 at 20°, 209 at 100°, and 222 at 118°, the boiling-

point of the saturated solution.   The solution, dissolves iodin readily
and also insoluble iodids forming double salts, such as $2KI, HgI_2$, or
$Hg < \begin{matrix} I = I - K \\ I = I - K \end{matrix}$.   It is much used as a medicine, especially in scrof-
ula and related diseases.

Potassium Cyanid, KCN, is prepared by saturating hydrocyanic
acid with potassium hydroxid or by strongly heating potassium
ferrocyanid:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

It is a white, very soluble solid of sharp, bitter taste.   It crystallizes
from solution in regular octahedrons and from fusion in cubes.   It
is unstable, being decomposed by all the acids, even carbonic, with
evolution of hydrogen cyanid.   It therefore smells of hydrocyanic
acid and is a violent poison.   It is used as a reducing agent and in
making the silver solutions used in photography.

Potassium Cyanate, KCNO, or $K—O—C≡N$, is a white crystalline
solid used in the preparation of certain organic compounds.

Potassium Thiocyanate, KCNS, forms deliquescent prismatic crystals
and is used as a refrigerant.   When 4 parts of water are added to 5 parts
of the salt the temperature sinks to $-20°$.

Oxids of Potassium.—Potassium forms five oxids, K_4O, K_2O,
K_2O_2, K_2O_3, K_2O_4.   Only one of these, K_2O, forms a hydroxid, and
the others may be regarded as radicals or loose compounds of potas-
sium or oxygen with K_2O.   All but K_2O are unstable and active
and readily pass into this compound.

Potassium Oxid, K_2O, is formed along with K_2O_4 when potas-
sium is burned in the air.   If the mixture be strongly heated the
K_2O_4 is decomposed and only K_2O is left.   It may also be prepared
by heating potassium hydroxid with potassium:

$$2KHO + 2K = 2K_2O + H_2.$$
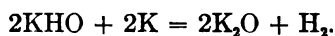
It is a gray brittle solid, very deliquescent and caustic, and unites
vigorously with water.

When potassium is melted in nitrogen, and this gradually replaced
by oxygen, it burns first to white K_2O_2 and then to yellow K_2O_4.   The
latter melts to a black liquid and decomposes at white heat.   It is a
powerful oxidizer, acting vigorously upon sulfur and phosphorus and
the metals generally and converting water into hydrogen peroxid.

Potassium Hydroxid, KHO, commonly known as *caustic potash,* is obtained by dissolving potassium or potassium oxid in water. The commercial article is prepared by adding lime to a boiling solution of potassium carbonate until a portion removed no longer yields CO_2 with acids:

$$CaH_2O_2 + K_2CO_3 = CaCO_3 + 2KHO.$$
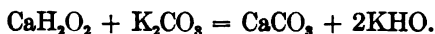
After the calcium carbonate subsides the clear liquid is poured off and evaporated in iron vessels until the specific gravity is 1.16, then in silver vessels until it solidifies on cooling. It is then moulded into sticks.

Potassium hydroxid is now prepared by electrolysis of strong potassium chlorid solution. The metal at the cathode acts with water to form KHO and free H, while chlorin escapes at the anode: $K^{\cdot}.Cl' + H_2O = K^{\cdot},HO' + H + Cl.$

Potassium hydroxid is a hard, brittle, white, deliquescent solid of specific gravity about 2.1. It melts below red heat and is volatile above this temperature. It dissolves vigorously in water in all proportions to a strong caustic solution whose strength may be determined by its specific gravity; e.g., 10 per cent 1.08, 20 per cent 1.18, 30 per cent 1.29, 40 per cent 1.4, 50 per cent 1.5, and 70 per cent 1.9. The strong solution is known as *potash lye,* and the *liquor potassæ* of the Pharmacopœia is a 5 per cent solution. Evaporated at a low temperature, crystals of $KHO,2H_2O$ are obtained. It also dissolves readily in alcohol. Ionization: $\dfrac{N}{100}$ 99 per cent; $\dfrac{N}{500}$ 100 per cent.

Potassium is the strongest commercial alkali. It destroys both vegetable and animal tissues and saponifies fat. For this reason it cannot be filtered through paper. The activity of the solution is due to the free potassium and hydroxyl ions K' and (HO)'. It dissolves glass and acts strongly with all the acids to form salts. It dissolves moisture and carbon dioxid from the atmosphere and is never free from the carbonate. It has a slippery, soapy feel, and is a powerful cleansing agent.

The chief use of potassium hydroxid is in the manufacture of soap which consists of potassium salts of the fatty acids, and is obtained by boiling fats with potassium hydroxid. It is used in the laboratory as an alkali and in organic analysis for absorbing carbon dioxid. Its use is somewhat limited because the cheaper sodium hydroxid may take its place in most operations.

Potassium Sulfid, K₂S, is obtained by reducing the sulfate with carbon or hydrogen: $K_2SO_4 + 4C = 4CO + K_2S$. The carbon must be used in excess, and even then the product is not free from higher sulfids.

Potassium sulfid is a red crystalline mass which absorbs moisture and oxygen from the air to form potassium thiosulfate, $2K_2S + H_2O + 4O = 2KHO + K_2S_2O_3$. It dissolves in water to the hydroxid and hydrosulfid, and the action is reversible: $K_2S + H_2O \rightleftharpoons KHO + KHS$. It dissolves in acids with evolution of hydrogen sulfid.

Potassium Polysulfids.—By action of sulfur upon potassium sulfid are formed the several polysulfids K_2S_2, K_2S_3, K_2S_4, K_2S_5. These are all colored and unstable, and may be regarded as loose compounds of potassium sulfid with sulfur or as thioacids of sulfur, such as potassium thiosulfite, K_2SS_2, corresponding to K_2SO_3. They all oxidize in the air to the ordinary potassium thiosulfate, the higher ones with separation of sulfur, $2K_2S_3 + 3O = K_2S + K_2S_2O_3 + S_3$.

Potassium Hydrosulfid.—As the hydroxid is obtained by the action of potassium upon water, so the hydrosulfid is formed when potassium acts upon hydrogen sulfid, hydrogen being evolved in both cases: $K + H_2S = H + KHS$. The solution is readily obtained by action of hydrogen sulfid upon potassium hydroxid: $KHO + H_2S = H_2O + KHS$.

Potassium hydrosulfid is a yellow solid which melts at redness and oxidizes gradually in the air to K_2S_2. The solution soon turns yellow from formation of higher sulfids, and finally becomes a colorless solution of the thiosulfate. On evaporation in vacuo crystals of $2KHS,H_2O$ separate.

Potassium Thiosalts.—Potassium sulfid and hydrosulfid combine with arsenic, antimony, and tin to form thiosalts, of which potassium thioarsenate, $2K_3AsS_4,9H_2O$, is an example.

Potassium Selenid, K₂Se, is formed by direct union of the elements. It is a steel-gray solid which decomposes water with evolution of hydrogen selenid.

Potassium Tellurid, K₂Te, is a crystalline copper-colored solid which yields hydrogen tellurid with acids.

Potassamin, KNH₂, is a yellow solid obtained by heating potassium in ammonia gas. It burns with scintillations and decomposes water, $KNH_2 + H_2O = NH_3 + KHO$.

Potassium Nitrid, K₃N, is a dark-green infusible solid obtained by ignition of potassamid, $3KNH_2 = 2H_3N + K_3N$.

Potassium forms rather indifinite and unstable compounds with phosphorus, arsenic, antimony, and bismuth, whose formulas are probably K_3P, K_3As, K_3Sb, and K_3B. They are unstable solids which are violently decomposed by water.

Potassium Salts.—Potassium is wholly basic and chemically

active and therefore forms salts with all the acids. These are nearly all soluble and dissociate in solution. They crystallize well, and many of them are of great commercial importance.

Potassium Hypochlorite, KClO.—A mixture of KCl and KClO is obtained by passing chlorin into dilute cold solution of KHO. This solution was formerly used for bleaching purposes under the name of *eau de Javelles*, from the bleaching works where it was first prepared.

Potassium Chlorate, $KClO_3$, may be prepared by action of chlorin upon potassium hydroxid: $6KHO + 3Cl_2 = 3H_2O + 5KCl + KClO_3$. Since only one sixth of the potassium is thus obtained as $KClO_3$, it is better to form first calcium chlorate and then decompose this with potassium chlorid. If chlorin be passed into milk of lime calcium hypochlorite is formed and this is converted by boiling into calcium chlorate. If now potassium chlorid be added, calcium chlorid and potassium chlorate are formed, $Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3$, and the two salts are separated by fractional crystallization.

Potassium chlorate is also prepared commercially by the electrolysis of strong hot solution of potassium chlorid, $KCl + 3H_2O = KClO_3 + 3H_2$.

Potassium chlorate crystallizes in large white monoclinic prisms, often iridescent, has a specific gravity 2.35 and a cooling, astringent taste. It melts quietly at 334° and at 352° evolves oxygen with brisk effervescence. One hundred parts water dissolve 3.3 parts at 0°, 6 parts at 18°, and 60 parts at 105°, the boiling-point of the saturated solution. It is a powerful oxidizing agent and makes explosive mixtures with combustibles. This may be shown by grinding a little with sulfur in a mortar or by igniting a mixture of sugar and the chlorate.

Potassium chlorate has various medicinal uses, but in large doses is an irritant poison. It is extensively used in the manufacture of oxygen, matches, and colored fires. The safety-match is tipped with a mixture of potassium chlorate and antimony sulfid, and the surface upon which it is rubbed is sand mixed with red phosphorus.

Potassium Perchlorate, $KClO_4$, is obtained by heating potassium chlorate until the liquid begins to solidify: $2KClO_3 = KClO_4 + KCl + O_2$. The very soluble KCl is dissolved away and the $KClO_4$ further purified by crystallization. At 400° it gives up all the oxygen. One part dissolves in 70 parts of water at 18° and in 6 parts at 100°.

Potassium Bromate, $KBrO_3$, Potassium Perbromate, $KBrO_4$, Potassium Iodate, KIO_3, and Potassium Periodate, KIO_4, have properties similar

to those of the corresponding chlorin compounds. Besides the last there are several hydrated periodates and diperiodates, such as $K_4IO_6,4H_2O$, the salt of the dimeta periodic acid H_4IO_6; and $K_4I_2O_9,9H_2O$, the salt of the diperiodic acid obtained by taking $5H_2O$ from two molecules of the hypothetical orthoperiodic acid $2H_7IO_7 - 5HO = H_4I_2O_9$.

Potassium Sulfites.—The three potassium sulfites may be prepared by action of sulfurous oxid upon potassium chlorate. When the CO_2 ceases to escape the solution contains the normal sufilte K_2SO_3. When the gas is passed to saturation the liquid contains $KHSO_3$, and when a hot solution is used the product is $K_2S_2O_5$. The last is more stable than the corresponding sodium salt and is used in photography.

Potassium Sulfate, K_2SO_4, occurs native as a double sulfate in *kainite*, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, particularly in the Stassfurt deposit, and as *polyhalite*, $K_2SO_4,MgSO_4,2CaSO_4,2H_2O$. It may be prepared from these minerals or by the action of sulfuric acid upon potassium chlorid: $H_2SO_4 + 2KCl = 2HCl + K_2SO_4$.

Potassium sulfate forms colorless anhydrous rhombic crystals of bitter, salty taste and specific gravity 2.6. It melts at 870° and dissolves in 10 parts of water. It is used as a purgative medicine, as a fertilizer, and in the manufacture of alum and potassium carbonate.

Potassium Hydrogen Sulfate, $KHSO_4$, is obtained by action of sulfuric acid upon nitrates, as in the laboratory method of preparing nitric acid. It forms rhombic crystals of specific gravity 2.3, melts at 200°, and dissolves in three parts of water.

Potassium Alum, Common Alum, $KAl(SO_4)_2,12H_2O$.—Alum is formed by the direct union of potassium and aluminum sulfates. It is prepared from clay and alum shales by treating them first with sulfuric acid and then with potassium sulfate.

Alum crystallizes in large octahedrons, often showing the faces of the cube. It has an astringent taste and dissolves in 100 parts of water 4 parts at 0°, 12 parts at 15°, and 357 parts at 100°. When heated it first melts in its water of crystallization, then loses the water and becomes a dry powder called *burnt alum.*

Alum has numerous applications in the arts. It is used in dyeing as a mordant, in paper-making, in calico-printing, and in clarifying muddy waters. It is a constituent of many baking-powders. It is not wholesome to man, and its internal use is to be avoided.

Potassium Chromic Sulfate (Chrome Alum), $KCr(SO_4)_2,12H_2O$, is obtained by reduction of potassium dichromate with sulfurous

oxid. The proper amount of sulfuric acid is added to a solution of the dichromate and the gas passed through the liquid. The reaction is as follows:

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = 2KCr(SO_4)_2 + H_2O.$$

Chrome alum crystallizes in dark-purple octahedrons which are red by transmitted light. It dissolves in seven parts of water to form a dingy reddish-blue solution which turns dark green at 70°. It is used in tanning, dyeing, and calico-printing.

Potassium Disulfate, $K_2S_2O_7$, is obtained by heating $KHSO_4$ to fusion. It crystallizes in needles which dissolve in water, forming again $KHSO_4$. At 600° it decomposes into sulfuric acid and sulfuric oxid.

Other salts are selenites, selenates, tellurites, and tellurates.

Potassium Chromate, K_2CrO_4, is obtained by adding potassium hydroxid to potassium dichromate solution:

$$K_2Cr_2O_7 + 2KHO = H_2O + 2K_2CrO_4.$$
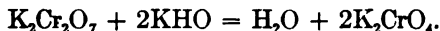
On evaporation it crystallizes in yellow, rhombic pyramids isomorphous with potassium sulfate and of specific gravity 2.7. One hundred parts of water dissolve 59 parts at 6°, 63 at 20°, and 79 at 100°. Acids convert it into the dichromate.

Potassium Dichromate, $K_2Cr_2O_7$, is formed when acids act upon potassium chromate:

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + H_2O + K_2Cr_2O_7.$$

Commercially the dichromate is prepared as follows: Pulverized chrome iron ore is heated with potassium carbonate and lime in a reverberatory furnace, whereby calcium and potassium chromates and iron trioxid are formed. The mass is extracted with hot water and potassium sulfate added to convert calcium chromate into potassium chromate. The clear solution, freed from the precipitated calcium sulfate, is treated with sulfuric acid as in the equation above.

Potassium dichromate forms large red triclinic prisms of specific gravity 2.7. It melts at 400° to a red liquid and decomposes at white heat: $3K_2Cr_2O_7 = Cr_2O_3 + 3O + 2K_2CrO_4$. One hundred parts of water dissolve 5 parts at 0°, 29 at 40°, 102 at 100°, and the saturated solution boils at 104°. It has a cooling, metallic taste and is a powerful poison. A gelatin film saturated with it is sensitive to light, the dichromate being reduced and the gelatin rendered insol-

uble. Because of this property it is used in certain photographic processes.

Potassium dichromate is the starting-point for the formation of nearly all the chromium compounds. It is used in dyeing and calico-printing and as an oxidizing agent. It reacts with sulfuric acid, giving up three atoms of oxygen:

$$K_2Cr_2O_7 + 4H_2SO_4 = 2KCr(SO_4)_2 + 4H_2O + 3O.$$

The nascent oxygen attacks any oxidizable substance which may be present.

Potassium Trichromate, $K_2Cr_3O_{10}$, and **Potassium Tetrachromate,** $K_2Cr_4O_{13}$, are red crystalline solids.

Potassium Chlorochromate, · $KClCrO_3$, or $\dfrac{K-O}{Cl} > CrO_2$, forms rectangular prisms.

Other salts of potassium belonging here are molybdates, polymolybdates, phosphomolybdates, tungstates, polytungstates, uranates, and peruranates.

Potassium Nitrite, KNO_2, is obtained by heating potassium nitrate along with lead, copper, or iron. The pure salt is prepared by decomposing silver nitrate with potassium chlorid. It forms deliquescent crystals and easily oxidizes to the nitrate. It is used in the separation of nickel and cobalt and in certain organic preparations.

Potassium Nitrate, KNO_3, is called *saltpeter,* the *sal petræ* of Geber, and *niter* from *nitrum,* the ancient name of soda. It is a constituent of all soils, and in hot climates appears as an efflorescence upon the surface. It is formed by the gradual oxidation of nitrogenous organic matters in the presence of potassium carbonate and through the action of certain bacteria, called nitrifying microbes. The process is carried on artificially in niter beds which are heaps of manure and animal matters mixed with wood-ashes and lime. It is also prepared by adding KCl to $NaNO_3$ solution, $K^{\cdot},Cl' + Na^{\cdot},NO_3' = Na^{\cdot}Cl' + K^{\cdot},NO_3'$. The salts are separated by crystallization.

Potassium nitrate is anhydrous and dimorphous. It usually crystallizes in rhombic prisms, but by slow evaporation small rhombohedral crystals are obtained. It has specific gravity 2.1, melts at 339°, and has a cooling, bitter, salty taste. It dissolves in water with absorption of heat, and the solubility increases rapidly as the temperature rises. One hundred parts of water dissolve 13 parts

at 0°, 31 at 20°, 86 at 50°, 247 at 100°, and 327.4 at 114°, the boiling-point of the saturated solution. It is unstable and a powerful oxidizer, and with combustibles makes explosive mixtures.

Niter is used as a medicine, as a meat preservative, and as the oxidizing agent in colored fires; but its chief use is in the manufacture of gunpowder, which, however, is now being replaced by the smokeless powders.

Gunpowder.—This is a granular mixture of niter, charcoal, and sulfur in about the proportion 75, 10, and 15, corresponding approximately to the following equation, which may be taken to represent the combustion of the powder:

$$2KNO_3 + S + 3C = K_2S + 3CO_2 + 2N.$$
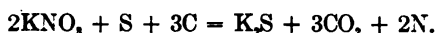
The reaction, however, is much more complex, and several other compounds are formed. The volume of the carbon dioxid and nitrogen at 0° is about 280 times, and at the temperature of the explosion, which may be 2000°, about 2000 times the volume of the powder. The pressure within the gun may reach 6000 atmospheres.

Potassium forms the usual salts with phosphorus, arsenic, and antimony, and there are vanadates, columbates, and tantalates.

Potassium Carbonate, K_2CO_3, commonly known as *potash*, is obtained from various sources:

1. *Wood-ashes.*—Until recently this was the chief source of potash. The solution obtained by leaching the ashes is evaporated in iron pots, hence the name *pot-ashes*. The residue contains also the chlorid, sulfate, and hydroxid, besides some sodium compounds. *Pearl-ash* is a purer product, obtained by separating during the evaporation the less soluble substances which crystallize first.

2. *Beet-root molasses.*—The molasses left from the beet sugar is rich in potash. This is fermented, evaporated, ignited, and extracted with water.

3. *Suint.*—Sheeps' wool is covered with an organic potassium salt derived from the perspiration, and called *suint*, which goes into solution when the wool is washed. The washings are evaporated, ignited, and extracted with water.

4. *Potassium sulfate.*—This is reduced with carbon, as in the Le Blanc process for soda. The sulfate is obtained from the native compound or by treating other salts, especially the chlorid, with sulfuric acid. The supply comes mainly from the Stassfurt beds and from the sulfate produced as a by-product in certain manu-

factures. The chemically pure salt is best obtained by igniting the pure acid carbonate.

' Potassium carbonate is a white deliquescent solid or powder, caustic and alkaline because of the hydrolysis which liberates the hydroxyl ion. It melts at 830° and is volatile at red heat. It crystallizes in monoclinic prisms with one and a half molecules of water. One hundred parts of water dissolve 90 parts at 0°, 112 at 20°, 140 at 80°, and 205 at 135°, the boiling-point of the saturated solution.

Potassium carbonate is used in the manufacture of soap and crystal or Bohemian glass and in the preparation of other compounds of potassium.

Potassium Hydrogen Carbonate, $KHCO_3$, known as *bicarbonate of potash,* is easily obtained in monoclinic crystals by passing carbon dioxid through potassium carbonate solution   It has a saline taste and faint alkaline reaction and dissolves in 3 parts of water. The salt decomposes at 110° and the solution on evaporation. The equation $2KHCO_3 \rightleftarrows K_2CO_3 + H_2O + CO_2$ is reversible and follows the phase law.

Potassium Fluosilicate,' K_2SiF_6, is formed by the action of fluosilicic acid upon a potassium salt. It is a white powder soluble in water.

Other · compounds that belong here are potassium fluogermanate, stannate, fluostannate, plumbate, titanate, fluotitanate, fluozirconate, fluothorate.

Potassium Silicates.—Silicic oxid and potassium carbonate melt together in all proportions to form a glassy mass, which dissolves in water to a viscid, transparent liquid called *potassium water-glass.* It has not a definite composition, but no doubt contains various potassium silicates. It is used in cotton-printing, color-fixing, and in fireproofing combustibles.

Potassium Metaborate, KBO_2, is obtained by fusing together boric acid and potassium carbonate. It forms monoclinic prisms.

Potassium Tetraborate, $K_2B_4O_7,5H_2O$, is obtained by adding potassium hydroxid to solution of boric acid. It crystallizes in hexagonal prisms and may be called *potash borax.*

Potassium Aluminate, $K_2Al_2O_4,3H_2O$, is obtained by fusing together in a silver dish aluminum oxid and potassium hydroxid.

RUBIDIUM.

Symbol Rb. Atomic weight 85.4. Valence I. Specific gravity 1.52. Melting-point 38.5°.

Occurrence.—Rubidium is very widely distributed, but in exceedingly

minute quantities.   It is found in sea and mineral waters, and in certain minerals, as lepidolite, porphorite, and carnallite.   Bunsen evaporated 40 tons of the Dürkheim water to obtain enough for the investigation of its properties.

History.—Rubidium was discovered by Bunsen, in 1861, by means of the spectroscope.   He named it *rubidium (red)*, referring to its spectrum, which contains two bright lines in the extreme red.

Preparation.—Rubidium is prepared by distilling a mixture of the hydroxid with magnesium or by reducing the carbonate, as in the preparation of potassium.   The mixture of carbon and carbonate is obtained by igniting rubidium tartrate.   The chief source of the metal is the residual liquids from the manufacture of the lithium and potassium compounds.

Properties.—Rubidium is a soft silver-white metal of specific gravity 1.52.   It melts at 38.5 and passes at red heat to a blue vapor.   Like potassium it forms an explosive compound with CO.   It inflames spontaneously in the air and decomposes water with violence.   In its properties and compounds it closely resembles sodium and potassium.

RUBIDIUM COMPOUNDS.

Rubidium is very active, and if the material were sufficiently abundant all the compounds could possibly be prepared which correspond to those of potassium and sodium.   It is the most strongly basic and most active of all the metals except cæsium.   Its valence is one, but it seems to form tri and penta halids.

Rubidium Hydrid, RbH, forms in colorless needles on heating Rb with H to 300°.

Rubidium Halids.—The halids of rubidium closely resemble those of potassium.   They form numerous double halids with one another, with other metals, and with the haloid acids.

Rubidium Oxid, Rb_2O, is a white powder obtained by burning rubidium.

Rubidium Hydroxid, $RbHO$, is prepared by dissolving the oxid in water, or, better, by adding barium hydroxid to a solution of rubidium sulfate.   It is a white deliquescent solid, more caustic than potassium hydroxid.

Rubidium Salts.—Rubidium forms salts with all the acids.   They are generally soluble, and crystallize well usually with water of crystallization.   They are chemical curiosities and none of them of commercial use.

CÆSIUM.

Symbol Cs.   Atomic weight 133.   Valence I.   Specific gravity 1.88. Melting-point 26°.

Occurrence.—Cæsium occurs along with rubidium, and, like it, is very

widely distributed, though in much smaller quantity. It is found in sea and mineral waters and in the ashes of tobacco, tea, coffee, and certain woods. The rare mineral *pollucite* contains 34 per cent of cæsium oxid.

History.—Bunsen, in 1860, discovered cæsium in the Drükheim waters. It was the first element discovered by means of the spectroscope. Bunsen named it *cæsium* (*blue*), referring to the fact that the spectrum contains two bright lines in the blue.

Preparation.—Cæsium is obtained by electrolysis of a mixture of cæsium cyanid and barium cyanid, or by reducing the hydroxid or carbonate with magnesium in a current of hydrogen.

Properties.—The properties of cæsium agree in the main with those of rubidium. Its exceeding rarity has prevented the thorough investigation of its compounds. It is a soft white metal of specific gravity 1.88, melts at 26°, and is more volatile than rubidium. It inflames spontaneously in the air and decomposes water with explosive violence. It is the most electro positive and the most active of all the metals.

CÆSIUM COMPOUNDS.

The cæsium compounds are exactly analagous to those of rubidium and need not be described.

AMMONIUM $(NH_4)'$.

The ammonium radical has already been treated in the chapter on the nitrogen group and its compounds have been described in connection with the elements or acids with which it combines. It remains only to call attention here to its close relationship with the alkali metals.

CHAPTER XXXVII.

GROUP I B. THE CUPROIDS. THE COPPER GROUP.

Copper 63.6. Silver 108. Gadolinium 156. Gold 197.

THESE elements are markedly different from the potassoids. They are much less positive, are scarcely alkaline, do not oxidize readily, and do not decompose water. Gold is even negative and forms aurates. They are strikingly similar to the metals of Group VIII, which they respectively follow. The usual gradation in physical properties is seen. In specific gravity, fusibility, malleability, ductility, tenacity, and hardness silver is intermediate between copper and gold. As the atomic weight increases the hardness, tenacity, and chemical activity diminish, and the fusibility, malleability, ductility, and electric conductivity increase. Chemically, they are not very active, gold least so. Copper, silver, and gold occur free in nature, and hence have been known from the earliest times. They are the metals (together with nickel) universally used for coinage. While the valence of the group is 1, copper acts also as a dyad, and gold as a triad.

Gadolinium is a rare and recently discovered element which is provisionally placed between silver and gold.

COPPER.

Symbol Cu. Atomic weight 63.6. Valence I and II. Specific gravity 8.95. Melting-point 1057°.

Occurrence.—Copper occurs free in nature, particularly where it has been liberated by volcanic agencies. Large deposits of this character are found in the vicinity of Lake Superior. It is usually massive, but sometimes in octahedral crystals. Combined copper is abundant and widely distributed.

The principal ores of copper are *cuprite* or *red copper ore*, Cu_2O; *melaconite* or *black copper ore*, CuO; *chalcocite* or *copper glance*,

Cu_2S; *covellite* or *indigo copper*, CuS; *chalcopyrite* or *copper pyrites*, $CuFeS_2$; *erubescite*, Cu_3FeS_3; *malachite*, $CuCO_3,Cu(HO)_2$, and *azurite*, $2CuCO_3,Cu(HO)_2$.

Rich copper mines are found in Michigan, Tennessee, California, Arizona, Montana, Colorado, New Mexico, Mexico, and various parts of the Old World.

History.—Copper was used by the earliest men. It is mentioned in the Bible, was called *chalcos* by the Greeks and *aes* by the Romans. The latter word meant also bronze or brass, and to distinguish them copper was called *aes cyprum*, because it came from the isle of Cyprus. Thus arose the name *cuprum*, from which the symbol of the element is taken. Copper was one of the seven ancient metals and was sacred to Venus.

Preparation.—For the preparation of copper there are three principal methods: (1) Reduction; (2) Chemical displacement; and (3) Electrolysis.

1. *Reduction.*—Copper is obtained from the oxids and carbonates by the simple reduction process of heating with carbon:

$$Cu_2O + C = CO + Cu_2.$$
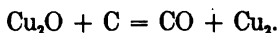
From the mixed ores containing sulfur the metal is not so easily extracted. In this case the ore is first roasted in the air to partially oxidize the sulfid. It is next fused, with addition of silicious matter if necessary, whereby the iron is oxidized and copper sulfid reformed:

$$Cu_2O + FeS = Cu_2S + FeO.$$
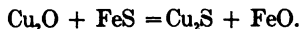
The iron oxid unites to the silica to form a fusible silicate which runs away, leaving a mixture of cuprous and ferrous sulfids called *coarse metal*, which contains 30 to 35 per cent of copper. This is again partially oxidized by roasting, and again fused with silicious flux to remove iron until a residue is obtained of nearly pure cuprous sulfid called *fine metal*, and containing 60 to 75 per cent of copper. This is partially oxidized by roasting and then reduced by heating:

$$2Cu_2O + Cu_2S = SO_2 + Cu_6.$$
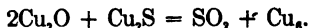
The copper thus obtained is called *blister copper*, and is refined by roasting to oxidize impurities, and then heating with carbon to reduce any copper that may have become oxidized.

2. *Chemical displacement.*—Copper is obtained in the wet way from ores poor in the metal, and especially from the burnt pyrite residue of the sulfuric acid manufacture, which contains about 3 per

cent of copper. The material may be treated in either of two ways: (1) It is calcined with common salt to form copper chlorid. This is dissolved out and the copper displaced with scrap iron. (2) The finely divided and moistened ore is allowed to oxidize in contact with the air. The ferric sulfate formed carries the copper with it into solution and the separation is again made with scrap iron.

3. *Electrolysis.*—Pure copper is best obtained by electrolytic deposition. Commercial copper in large plates is made the anode in a bath of copper sulfate, while the cathode is a thin sheet of copper foil. The metal is transferred from the anode to the cathode by a strong electric current. Metallic impurities, such as silver, gold, antimony, tin, bismuth, fall at the anode; arsenic goes partly into solution and is removed from time to time by boiling as ferric arsenate.

Physical Properties.—Copper is a moderately hard, lustrous metal of a peculiar color known as copper-red. It is quite malleable and ductile and has a tenacity considerably below that of iron. Its malleability and ductility are greatly diminished by admixture with other metals. When heated nearly to the melting-point it is brittle and may be powdered. It melts at 1057° and distils in the electric arc, yielding a green vapor. When liquid it absorbs gases which it gives out on cooling, with *spitting*. The specific gravity of electrolytic copper is 8.945 and of hammered copper 8.95. Copper is a good conductor of heat and the best conductor of electricity after silver.

Chemical Properties.—Copper is quite permanent in dry air, but in moist air it becomes covered with a greenish coating of basic copper carbonate (verdegris). When heated it oxidizes rapidly, forming surface scales of a mixture of cuprous and cupric oxids. It dissolves in nitric acid to copper nitrate, with evolution of oxids of nitrogen. Cold sulfuric and hydrochloric acids do not attack it, but when heated the former gives copper sulfate and sulfurous oxid, and the latter cuprous chlorid and hydrogen. It dissolves in ammonia, in the presence of the air, to a blue solution. It unites directly to chlorin, and, when heated, to sulfur. In the presence of air it is attacked by various food materials, and hence is not suitable for cooking-utensils. Its salts are poisonous, but rarely produce death.

Uses.—Copper is extensively used as wire for conducting the

electric current, as sheet copper, as material for coins and electro-type plates, and in alloys, the chief of which is brass.

The consumption of copper has greatly increased in the last few years because of the large quantity used in electric appliances. The copper mines of the West, particularly those of Arizona and Colorado, have added greatly to the wealth of our country. Copper is worth about 15 cents a pound.

Alloys of Copper.—No alloys are more important than those of copper. They are valuable on account of their hardness, toughness, malleability, ductility, gold-like color and luster, and capability of taking fine polish. The principal combinations are with zinc, tin lead, iron, alumirrum, nickel, silver, and gold. With zinc it forms brass, muntz metal, and tombac; with tin, bronze, bell metal, and mirror bronze; with tin and zinc, statue bronze, coin bronze, imitation gold, and Talmigold; with iron and zinc, delta metal; with aluminum, aluminum bronze; with tin, zinc, and phosphorus, phosphor bronze; with nickel, coin; with silver, coin and silver plate; with iron, sheets coated on one or both sides with copper.

A few examples are given to show the relative amounts of the metals in various alloys:

	Copper.	Zinc.	Tin.		Copper.	Zinc.	Tin.
Brass..........	6€	34		Muntz metal....	75	25	
Tombac........	87	13		Gun metal.....	90	..	10
Bronze........	84	10	6	U. S. coin.....	95	2	3

The above proportions may generally be varied within large limits. Other copper alloys are mentioned elsewhere.

Electrotyping.—If a sheet of zinc is suspended in a solution of copper sulfate, it presently becomes covered with copper. If the electrodes of a battery are placed in the solution and a current passed, the copper is deposited upon the cathode or negative electrode. If both electrodes are made of copper, the metal is gradually transferred from the anode to the cathode. The copper thus deposited is firm and compact and the process is called *copper-plating* or *electrotyping*. If the object to be covered is not a conductor, it is made one by being dusted over with a thin layer of graphite. The deposition is continued until the sheet of copper is thick enough to

bear handling. On the mould or negative thus obtained another deposit is made which is a copy of the object. It is in this way that copper copies of statues, wood-cuts, etc., are made.

COPPER COMPOUNDS.

Copper is chemically rather active and forms numerous compounds. It is usually bivalent, having its closest relationship with zinc instead of the alkali metals, and in solution the elementary ion is $Cu^{..}$, usually blue. It acts also with an apparent valence I, but the univalent ion $Cu^{.}$ is not separable and cuprous oxid dissolves in acids to cupric salts. The formulas are therefore usually written so as to contain two atoms of copper connected together, as Cu_2Cl_2 or $Cl-Cu-Cu-Cl$, and Cu_2O or $Cu-Cu$ with O below.

The thermal equations for a few of the copper compounds are:

$(Cu,Cl_2) = 51,600$ cal. $(Cu_2,Cl_2) = 65,700$ cal. $(Cu,S,O_4) = 182,600$ cal.
$(Cu,O) = 37,200$ cal. $(Cu_2,O) = 40,800$ cal. $(Cu_2,S) = 18,300$ cal.

Copper Halids.—Copper forms cuprous and cupric halids which have the general properties of copper salts.

Cuprous Fluorid, Cu_2F_2, is a red powder formed by action of hydro-fluoric acid upon cupric hydroxid.

Cupric Fluorid, CuF_2, is a blue crystalline solid obtained by dissolving cuprous oxid in hydrofluoric acid. At 100° it yields the oxyfluorid $CuF(HO)$.

Cuprous Chlorid, Cu_2Cl_2, is prepared by action of hydrochloric acid upon cupric chlorid in the presence of finely divided copper. The nascent hydrogen formed by action of copper upon hydrogen chlorid reduces the cupric to cuprous chlorid. On pouring the solution into water the cuprous chlorid separates as a white crystalline precipitate (tetrahedrons).

Cuprous chlorid melts at 430° and volatilizes at about 1000°. It is insoluble in water, soluble in hydrochloric acid, ammonia, and alkali chlorids. In moist air it turns green, changing to $CuCl(OH)$. When heated in the air, it oxidizes to *cuprous oxychlorid*, Cu_2Cl_2O, which in turn is decomposed at 400°, giving off the oxygen. This action has been used for the preparation of oxygen.

Cupric Chlorid, $CuCl_2$, is obtained by heating copper in chlorin, or by dissolving it in *aqua regia*, or by dissolving cupric oxid, car-

bonate or hydroxid in hydrochloric acid. It is a dark, yellowish-brown deliquescent solid with a caustic, metallic taste. It dissolves in water to a green solution, from which it crystallizes in rhombic prisms of $CuCl_2,2H_2O$. The dilute solution is blue, because of the blue copper ion. It is also soluble in alcohol and ether. When heated it dissociates into cuprous chlorid and chlorin. It absorbs ammonia, forming three or more definite compounds.

Several oxychlorids result from the action of chlorin compounds upon copper in the presence of water and oxygen. The most important is $Cu_2Cl(HO)_3$, which occurs native in Chili and Peru as the mineral *atacamite* and comes in commerce as *Brunswick green*.

Cuprous Bromid, Cu_2Br_2, is a brown crystalline solid obtained by heating copper with bromin.

Cupric Bromid, $CuBr_2$, is a deliquescent, crystalline solid which separates from solution of cupric oxid in hydrobromic acid.

Cuprous Iodid, Cu_2I_2, is a white crystalline powder obtained by heating copper with iodin or hydriodic acid, or by action of potassium iodid upon a cupric salt.

Cuprous Cyanid, $Cu_2(CN)_2$, is a white solid obtained by heating cupric cyanid or by action of potassium cyanid upon cupric chlorid.

Cupric Cyanid, $Cu(CN)_2$, is thrown down as a red precipitate when potassium cyanid solution is added to solution of copper sulfate.

Cuprous Thiocyanate, $Cu_2(SCN)_2$, is a white solid obtained by action of ferrous sulfate upon cupric thiocyanate.

Cupric Thiocyanate, $Cu(SCN)_2$, falls as a black precipitate when potassium thiocyanate is added to copper sulfate solution.

Cuprous Oxid, Cu_2O, occurs native as *cuprite* or *red copper ore* in octahedrons and massive. It may be prepared by melting together cuprous chlorid and sodium carbonate and dissolving away the sodium chlorid:

$$Cu_2Cl_2 + Na_2CO_3 = 2NaCl + CO_2 + Cu_2O.$$
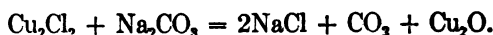
It is precipitated by the reducing action of grape-sugar upon alkaline copper solutions. This action is used for the detection and determination of sugar, particularly in urinalysis.

Cuprous oxid is a red powder insoluble in water, soluble in acids. It fuses at red heat and imparts a ruby-red color to glass.

Cuprous Hydroxid, $Cu_2(HO)_2$, is formed by reduction of alkaline copper solution in the cold or by action of alkali hydroxids and carbonates upon cuprous chlorid. It is a yellow powder which

dissolves in ammonia to a colorless liquid which soon turns blue from formation of cupric compounds.

Cupric Oxid, CuO, occurs native as *melaconite* massive or in black orthorhombic crystals. It is prepared by burning copper in air or oxygen or by igniting the nitrate, carbonate, or hydroxid. It is a black powder insoluble in water, soluble in acids. It is easily reduced by carbon, hydrogen, or organic matters, and hence is a good oxidizing agent. It is commonly used as such in organic analysis.

· **Cupric Hydroxid,** $Cu(HO)_2$, falls as a pale-blue precipitate when alkali hydroxids are added to solutions of cupric salts. At 100° it loses water and becomes cupric oxid. It dissolves in acids to cupric salts and in ammonia to a blue solution which dissolves cellulose (wood-fibre, cotton, etc.) and contains the ion $Cu(NH_3)_4$.

Cuprous Sulfid, Cu_2S, occurs native as *chalcocite* or *copper glance* massive and in gray orthorhombic prisms of specific gravity 5.6. It is formed when sulfur is heated with copper in excess. It combines with iron sulfid in several proportions, occurring thus in the minerals *chalcopyrite*, $CuFeS_2$, and *bornite*, $CuFeS_3$.

Cupric Sulfid, CuS, occurs native as *covellite* or *indigo copper* in blue hexagonal crystals. It is prepared by heating copper with sulfur in excess. It falls as a black precipitate when hydrogen sulfid is added to a cupric solution. This precipitate oxidizes easily on exposure to air or heat.

Cuprous Selenid, Cu_2Se, occurs native in *berzelianite* and as a constituent of *eucairite,* $(CuAg)_2Se$, *crooksite,* $(Cu_2TlAg)_2Se$, and *zorgite,* $(PbCu)Se$.

Copper and the Nitroids.—Copper forms alloys or indefinite compounds with nitrogen, phosphorus, and arsenic. The compounds Cu_6N_2, Cu_6P_2, and Cu_3P are described. Copper and arsenic enter together into the composition of a number of minerals, and the elements melt together in various proportions.

Copper Carbid or **Copper Acetylid,** Cu_2C_2, is obtained by treating alkaline solution of cuprous oxid with acetylene gas. When freshly prepared and dried in vacuo it is highly explosive. On exposure to the air it polymerizes and becomes more stable.

Copper Silicid, Cu_2Si, is prepared by fusing copper with silicon in the electric furnace. It is a crystalline solid of specific gravity 6.9.

Copper Salts.—Cuprous salts are not numerous, since they are unstable and easily pass to cupric forms.

Anhydrous cupric salts are yellow or colorless, while the hydrous forms are generally green or blue.   The normal salts are soluble in water, the basic salts insoluble.   All are poisonous.   They combine with ammonia to form various peculiar compounds.   Double salts are also quite common.
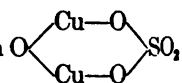
Cuprous Sulfite, Cu_2SO_3,H_2O, separates in red rectangular prisms when sulfurous oxid is passed through a mixture of water and ammonium cuprous sulfite.

Ammonium Cuprous Sulfite, $(NH_4)_2SO_3,Cu_2SO_3,$ falls in colorless scales when ammonium sulfite and copper sulfate are mixed.
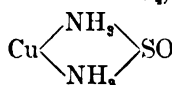
Cupric Sulfate, $CuSO_4,5H_2O$, is the common salt known as *blue vitriol* or simply *copper sulfate*.   It occurs to a limited extent in nature as the result of the oxidation of copper pyrites, and is prepared on a large scale from this mineral.   It may be obtained by dissolving copper in sulfuric acid.   It is also a secondary product of the refining of silver.

Copper sulfate forms large blue triclinic crystals which are slightly efflorescent and dissolve in water, one part to three at 10° and two parts to one at 100°.   It loses four molecules of its water at 100° and the remaining molecule at 250°.   The anhydrous salt is colorless, but absorbs moisture rapidly, becoming hydrous and blue. At red heat it separates into SO_2,O and CuO.   It forms double salts with the alkali metals which crystallize with $6H_2O$ and are isomorphous with the double magnesium sulfates.

Copper sulfate is the most important of all the copper compounds. It is used in calico-printing, in electroplating, in the manufacture of copper pigments, in galvanic batteries, as a preservative of wood, and as a fungicide.

Several basic copper sulfates are known, of which $O\diagdown\begin{smallmatrix}Cu-O\\ Cu-O\end{smallmatrix}\diagup SO_2$ may be taken as an example.

Cuprammonium Sulfates.—When alcohol is added to a solution of copper sulfate in strong ammonia, blue crystals of $CuSO_4,4NH_3,$ H_2O separate.   At 150° this salt gives off its water and $2NH_3$ and leaves $CuSO_4,2NH_3$, which is supposed to have the structure $Cu\diagup{}^{NH_3}_{NH_3}\diagdown SO_4$.   Other copper salts act in a similar way.

Copper Nitrate, $Cu(NO_3)_2 6H_2O$, is prepared by dissolving copper or copper oxid in dilute nitric acid and evaporating. It forms blue, prismatic crystals, which melt at 26°, losing $3H_2O$, and at a higher temperature decompose. It is deliquescent, very soluble, and a powerful oxidizer. It is used in dyeing and calico-printing.

Copper Phosphate, $Cu_3(PO_4)_2 3H_2O$, falls as a bluish-green powder when a copper solution is treated with phosphoric acid or sodium phosphate.

There are several basic copper phosphates which occur native, as *libethenite*, $PO_4(CuOH)Cu$, and *phosphochalcite*, $PO_4(CuOH)_3$.

Copper Arsenite, $CuHAsO_3$, falls as a green precipitate when potassium or sodium arsenite is added to a copper solution. It is used as a pigment under the name of *Scheele's green. Paris green* is a mixed arsenite and acetate of copper.

Copper Arsenate, $Cu_3(AsO_4)_2, 2H_2O$, is obtained as a blue powder by heating copper nitrate with calcium arsenate. Several basic arsenates occur native, as *olivenite*, $Cu(CuOH)AsO_4$, and *clinoclasite*, $AsO_4(CuOH)_3$.

Copper Carbonates.—Neutral copper carbonate has not been prepared. Several basic carbonates are known, two of which occur native and are of special interest.

Malachite, $CO_3(CuOH)_2$, found in the Altai and Ural Mountains, is of a beautiful variegated green color, takes a fine polish, and furnishes material for works of ornament and art (table tops, vases, etc.). The compound may be prepared artificially by treating a warm copper solution with an alkali carbonate. It is this substance which forms on copper articles, particularly in the presence of grease, and is known as *verdigris*.

Azurite, $O < \begin{matrix} CO-O-CuOH \\ CO-O-CuOH \end{matrix}$, occurs in azure-blue crystals and masses. It is used as an ornament and as a pigment.

Copper Silicates.—Two silicates of copper occur in nature: *dioptase*, CuH_2SiO_4, in emerald-green crystals, and *chrysocolla*, CuH_2SiO_4, H_2O, in blue, botryoidal masses.

SILVER.

Symbol Ag. Atomic weight 108. Valence I. Specific gravity 10.56. Melting-point 954°. Specific heat 0.057.

Occurrence.—Silver occurs native in considerable quantity. In the museum at Copenhagen is a mass found in Norway which weighs 500 pounds, and still larger masses have been found in Peru. Native silver usually contains gold and sometimes copper and other metals.

The common ores of silver are *argentite* or *silver glance*, Ag_2S;

pyrargyrite or *ruby silver ore*, Ag_3SbS_3; *proustite*, Ag_3AsS_3; *polybasite*, Ag_9SbS_6; *stromeyerite*, $AgCuS$; *horn silver*, $AgCl$; *silver bromid*, $AgBr$; *silver iodid*, AgI; and *hessite*, Ag_2Te.

Silver is also found in native gold and in many ores of other metals, notably in galena, PbS, which is one of the chief sources of silver.

History.—Silver was known to the ancients, and has always been used for coins and for articles of ornament. The name *silver* is a modification of the Anglo-Saxon word *seolfer*. The Romans called it *argentum*, from its Greek name *arguros*, which means *shining*, and from this the symbol is taken. Silver was assigned to the moon by the alchemists and was called *Luna* and also *Diana*.

Preparation.—Silver chlorid is decomposed by iron, lead, or mercury. Silver sulfid is converted into the chlorid by roasting with sodium chlorid. Silver is displaced from its solutions by zinc, iron, copper, mercury, and lead. The separated silver may be taken up with mercury and then freed from it by distillation.

Refining of Silver.—All silver obtained from native ores, as well as commercial silver, contains other metals, especially lead, copper, gold, and platinum. From lead and copper it is separated by *cupellation*, and form gold and platinum by *parting*. In cupellation the alloy is heated with free access of air, in a cupel, a vessel made of bone-ash. The oxids of lead and copper are partly volatilized and partly absorbed by the bone-ash and the silver-gold-platinum alloy remains as a button on the cupel. In parting, the button, which must contain about two parts of silver to one of gold, is rolled into a thin sheet and treated with nitric or sulfuric acid. The silver dissolves, leaving the gold and platinum, and is displaced from the solution with iron or copper.

For the further purification of the silver there are two processes, one chemical and the other electrolytic. In the first the last operation mentioned above is repeated and the precipitated silver washed and melted into bars. In the electrolytic method plates of silver are made the anodes in nitric acid solution of silver nitrate containing a little copper nitrate to make it a better conductor. The cathode is a thin sheet of silver. When the current is passed, the metal is transferred from anode to cathode and deposited in large crystals of pure silver, which are continually removed to prevent short currents.

Metallurgy of Silver.—There are various processes of obtaining silver from its ores, but they may all be included under three heads: (1) The amalgamation process; (2) the lead process; (3) the wet processes.

The amalgamation process.—In this process the ground ores, which have been roasted with or without salt, are treated with mercury. The silver amalgam is strained through canvas or chamois-skin bags to remove the excess of mercury and then distilled.

The lead process.—The lead process is used when the ores contain both silver and lead. The alloy of lead and silver obtained by reducing or smelting the ores is cupelled. If the alloy is not rich in silver, it is concentrated by the *Pattinson process* or the *Parkes process.* In the first the alloy is melted and cooled. Lead, having a higher melting-point than the alloy, solidifies first and is removed as fast as the crystals form. By repeating the operation a rich alloy is obtained which is then cupelled. In the Parkes process zinc is added to the fused metal. The zinc takes the silver, and the zinc-silver alloy rising to the top solidifies first and is removed. This mixture of zinc, silver, and lead is *liquated;* that is, heated until the lead melts and flows away from the less fusible zinc-silver alloy. The residue is distilled to remove zinc and cupelled to remove lead.

The wet processes.—In the *Ziervogel process* the sulfur-containing ores are roasted until most of the baser metals are oxidized, the silver sulfate is dissolved out with water and the silver precipitated with copper. In the *Percy-Patera process* the ore is roasted with salt, the silver chlorid dissolved out with sodium thiosulfate, the silver sulfid precipitated with sodium or calcium sulfid, and reduced by roasting in a reverberatory furnace.

Physical Properties.—Silver is a white lustrous metal somewhat harder than gold, but softer than copper. It is quite malleable, and very ductile and tenacious. Thin leaves transmit a bluish-green light. It melts at 954° and distils in the oxyhydrogen flame or electric arc, yielding a green vapor. Fused silver dissolves twenty times its volume of oxygen and on cooling emits it with *spitting.* Silver has specific gravity when cast 10.42, when hammered or distilled 10.57. It is the best conductor of heat and electricity.

Besides the ordinary metallic silver there are two other forms, probably allotropes, called *molecular silver* and *colloidal silver.*

Molecular silver is obtained as a very fine powder by reducing freshly precipitated silver chlorid with formaldehyde in the presence of potassium carbonate.

Colloidal silver is obtained by heating to 100° silver citrate in a stream of hydrogen or by passing an electric current between silver electrodes in water. It dissolves in water to a red solution which

does not dialyze. A gold-colored modification may also be obtained. Both these forms are converted into ordinary silver by fusion.

Chemical Properties.—Silver is unchanged in pure air, but tarnishes quickly in the presence of hydrogen sulfid from formation of silver sulfid. For the same reason it is blackened by substances containing sulfur compounds such as mustard and eggs. It is not attacked by alkalis, but unites directly to the halogens. It dissolves in nitric acid and hot sulfuric acid, forming the nitrate and sulfate, with reactions similar to those of copper:

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O.$$
$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$
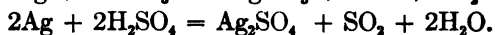
Silver Alloys.—Silver alloys readily with many metals. Arsenic, antimony, bismuth, tin, and zinc render it brittle. With lead, copper, aluminum, gold, and platinum it forms perfect alloys in almost all proportions. The copper-silver alloy is the one most used. It melts at a temperature below the melting-point of copper or silver, is hard, malleable, and ductile, and has the color and luster of the predominating metal.

Uses.—Pure silver is used in certain analytical chemical processes, in assaying, and in the manufacture of crucibles. Impure silver and copper-silver alloys are used for a multitude of purposes. The silver coin of the United States contains 9 parts of silver to one of copper; that of England has 925 silver to 75 copper. Sterling silver has the composition of English coin. The silver of tableware, jewelry, and works of art varies in fineness from 750 to 950 parts in 1000. Alloys high in copper may be whitened as follows: The metal is heated to oxidize the surface copper, then treated with acid to dissolve away the copper oxid. This leaves a rough surface called *frosted silver*. Under polish, the surface assumes the color and luster of pure silver.

The price of silver varies with the supply, and within a few years has so fallen that it is no longer a standard of money value. It is worth now (1904) 54 cents an ounce, or 42 cents to the dollar. The silver dollar weighs 412.5 grains and contains 371.25 grains pure silver.

Molecular silver is chemically more active than ordinary silver

and is used in the synthesis of certain organic compounds. Colloidal silver finds application in surgery.

Silver-plating and Silvering.—Silver is much used as a covering for other metals and as a coating for backs of mirrors. If the coat is thick it is called *silver-plating*; if thin, *silvering*. The process is conducted in various ways.

In silver-plating of copper the clean plates of copper and silver are laid together, brought near to the melting-point and passed between rollers.

In electro-plating a bath of potassium silver cyanid is used. The object to be plated is made the cathode and the anode is a plate of silver.

In hot silvering the surface of the metal is covered with silver amalgam and then heated to drive off the mercury.

In cold or dry silvering a mixture of silver chlorid, sodium chlorid, potash, and chalk is rubbed upon the surface of the metal until the silver coating is of sufficient thickness.   Other mixtures are also used.

In wet silvering the metallic object is dipped into a silver solution obtained in various ways. A good solution for small objects like pins and buttons is sodium chlorid, silver chlorid, and cream of tartar.

Glass is silvered by dipping it, well cleaned, in an ammoniacal solution of silver nitrate to which has been added caustic soda and some reducing agent, as rochelle salts, milk-sugar, aldehyde ammonia, etc.   In a few minutes the glass is covered with a continuous uniform and highly polished coating of precipitated silver. The coat is varnished to make it permanent. This method of making mirrors is replacing the tin-amalgam method.

SILVER COMPOUNDS.

Silver is less active than copper, but still forms numerous compounds. It unites readily with many organic radicals. It is wholly positive and univalent, yielding but one elementary ion, $Ag^{\cdot}$. Many of its compounds are decomposed by heat, leaving metallic silver. A few are volatile, like silver chlorid.

Some of the thermal equations are as follows:

$(Ag,Cl) = 29{,}400$ cal. $(Ag,Br) = 22{,}700$ cal. $(Ag,I) = 13{,}800$ cal.

$(Ag_2,O) = 5{,}900$ cal. $(Ag_2,S) = 3{,}300$ cal. $(Ag,N,O_3) = 28{,}700$ cal.

$(Ag_2,S,O_4) = 167{,}300$ cal. $(Ag_2,C,O_3 = 122{,}900$ cal.
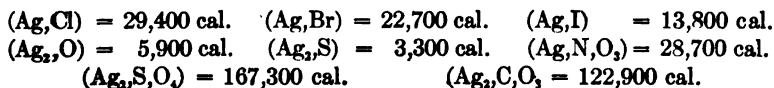
Silver Halids. —Silver possesses a strong affinity for the halogens and the halogen-like radicals, and forms compounds with them which are decomposed by light, with deposition of silver. There are many double halids, like $AgK(CN)_2$.

Silver Fluorid, AgF, is obtained by dissolving silver oxid or carbonate in hydrofluoric acid. It crystallizes with one or two molecules of water, from which it cannot be wholly freed. It absorbs dry ammonia in large quantity.

Silver Chlorid, AgCl, occurs native in octahedral crystals of *cerargyrite*, also in wax-like masses of milky or gray color, called *horn silver*. It is formed by action of chlorin or chlorids upon silver and most silver compounds. It is a white amorphous solid of specific gravity 5.5. It turns yellow when heated, melts at 480°, and becomes vapor at red heat. It is insoluble in water and acids, but dissolves in ammonia, in soluble chlorids and cyanids, and in potassium thiosulfate. It darkens on exposure to light, from separation of silver, and is reduced by metals and reducing agents. It crystallizes from solution in ammonia as $2AgCl,3NH_3$.

Silver Bromid, AgBr, is found in Mexico and Chili as *bromargyrite* or *green silver*. It is thrown down by bromids from silver solutions as a yellow precipitate. It melts easily to a red liquid and decomposes at a higher temperature. It is insoluble in water and acids and slightly soluble in ammonia and thiosulfates. It is very sensitive to light and is the chief substance used in dry-plate photography.

Silver Bromchlorid, Ag_2BrCl, occurs in Chili and Mexico as the mineral *embolite*.

Silver Iodid, AgI, is found in Mexieo, Chili, Spain, and Arizona as the mineral *iodargyrite*. It is formed by direct union or by action of soluble iodids on silver solutions. It is a yellow solid which has specific gravity 5.7, and melts at dull-red heat. It is insoluble in water and most acids. It dissolves in hydriodic acid and in strong solution of potassium iodid to form the double salts $HAgI_2$ and $KAgI_2$, which separate in colorless crystals. It is scarcely soluble in ammonia, a property which serves for its separation from the other silver halids. It is more stable than the chlorid or bromid and less sensitive to light.

Silver Cyanid, AgCN, is precipitated from silver solutions by soluble cyanids as a white curdy solid. It dissolves in ammonia

and alkaline cyanids to form double salts such as *potassium silver cyanid*, $KAg(CN)_2$, which is used in electro silver-plating.

Silver Cyanate, $AgOCN$, and **Silver Sulphocyanate,** $AgSCN$, are white solids soluble in ammonia.

Photography.—The science and art of photography are based upon the sensitiveness of silver halids to light. The process is essentially as follows:

1. A film is formed on a glass plate by covering it with collodion containing chlorid and bromid of copper or cadmium. This is rendered sensitive by dipping it in a solution of silver nitrate, whereby silver chlorid and bromid are formed in the film.

2. The sensitive plate, from which light must be carefully excluded, is placed in the camera and exposed to the image of the object to be photographed. The light decomposes the chlorid and bromid of silver in proportion to its intensity.

3. The plate, upon which no image is yet visible, is immersed in the "developer," usually a solution of ferrous sulfate or pyrogallic acid. This causes a further decomposition of the halids and the deposition of metallic silver, which brings out or develops the picture.

4. When the development has reached the proper stage the plate is immersed in a solution of sodium thiosulfite, commonly called "hypo," which dissolves away the unchanged halids and "fixes" the picture or makes it permanent.

5. The picture thus obtained is a "negative"; that is, the parts are reversed and the lights are where the shades are in the original. The "positive" picture is made by placing the negative over a sheet of sensitized paper and exposing it to the light and then developing and fixing as above.

6. This picture has an ugly brown tint and to make it more pleasing it is "toned." Before fixing, the picture is dipped in a solution of gold chlorid, whereby a little gold is precipitated along with the silver, which causes the color to remain gray or bluish after fixing.

7. The sheet of paper is then dried and mounted on cardboard.

Silver Oxid, Ag_2O, is obtained by heating silver in oxygen to 300° under a pressure of 15 atmospheres. It is also obtained not quite anhydrous by gently heating the hydroxid. It is a brown powder of specific gravity about 8. It decomposes at 260° and is a powerful oxidizer. It dissolves in ammonia, and the solution deposits unstable black crystals of a substance which is probably silver amid, $AgNH_2$. This is Berthollet's fulminating silver.

Silver Hydroxid, AgHO, falls as a white precipitate when alcoholic potash is added to alcoholic solution of silver nitrate at $-$ 40°. When precipitated at ordinary temperature it is gray or brown from formation of silver oxid. It dissolves in much water to a colorless alkaline solution.

Silver Peroxid, Ag_2O_2, is obtained by action of ozone upon moist silver or by electrolysis of silver solutions. It forms black octahedral crystals which lose oxygen when gently warmed. It is a more powerful oxidizer than silver oxid and detonates with sulfur or phosphorus. It dissolves in nitric acid to a powerful oxidizing solution.

Silver Sulfid, Ag_2S, occurs native as *argentite* or *silver glance* in regular octahedrons of gray color. It is formed by direct union or by action of soluble sulfids upon silver or silver solutions. This is the cause of the blackening of silverware in air containing hydrogen sulfid or in sulfur-bearing foods, like eggs and mustard. Silver articles are often purposely darkened in this way, and this is called *oxidized silver.* Silver sulfid is insoluble in water and ammonia, but dissolves in nitric acid.

Silver Persulfid, Ag_2S_2, has been obtained as a black amorphous powder by adding a solution of silver nitrate in benzonitril to a solution of sulfur in carbon disulfid.

Silver Selenid, Ag_2Se, and **Silver Tellurid,** Ag_2Te, occur along with the sulfids of silver and other metals in a number of minerals.

Silver Nitrid or **Silver Hydrazoate,** AgN_3, is the silver salt of hydrazoic acid, HN_3. It resembles silver chlorid, may be melted if carefully heated, and is fearfully explosive.

Silver Salts.—Silver salts are all more or less unstable, being especially sensitive to light rich in actinic rays. They yield with alkali hydroxids Ag_2O, with alkali cyanids the ion $Ag(CN)_2'$, with ammonium hydroxid $Ag(NH_3)_2\cdot$, with thiosulfates $AgSSO_3\cdot$.

Silver Chlorite, $AgClO_2$, crystalline powder obtained by action of an alkaline chlorite upon silver nitrate.

Silver Chlorate, $AgClO_3$, white quadratic prisms of specific gravity 4.43, obtained by dissolving silver oxid in chloric acid.

Silver Bromate, $AgBrO_3$, efflorescent needles.

Silver Iodate, $AgIO_3$, monoclinic crystals.

Silver Sulfite, Ag_2SO_3, is precipitated from silver solutions by sulfurous acid as a white, unstable solid.

Silver Sulfate, Ag_2SO_4, is prepared by dissolving silver in hot sulfuric acid and evaporating. It forms shining rhombic crystals of specific gravity 5.4. It is the common intermediate product in silver refining. It unites with aluminum sulfate to form *silver alum*, $AgAl(SO_4)_2,12H_2O$.

Silver Thiosulfate, $Ag_2S_2O_3$, is a white unstable powder of sweet taste, obtained by action of sodium thiosulfate in excess upon silver nitrate.

Sodium Silver Thiosulfate, $NaAgS_2O_3$, silky scales.

Silver Chromate, Ag_2CrO_4, is formed by action of potassium chromate upon silver nitrate. It is a red crystalline powder insoluble in water, soluble in ammonia, nitric acid, and alkali chromates.

Silver Dichromate, $Ag_2Cr_2O_7$, scarlet crystals, obtained by adding potassium dichromate to silver solutions.

Silver Hyponitrite, $AgNO$, falls as a yellow precipitate when an ethereal solution of hyponitrous acid is added to a solution of silver nitrate containing sodium acetate.

Silver Nitrite, $AgNO_2$, is a white crystalline powder obtained by mixing warm solutions of silver nitrate and sodium nitrite or by boiling a mixture of silver nitrate and powdered silver. It forms large white rhombic prisms.

Silver Nitrate, $AgNO_3$, is prepared by dissolving silver in nitric acid and evaporating. It forms large colorless rhombic prisms of specific gravity 4.33. It is quite soluble, 100 parts of water dissolving cold 122 parts, boiling 1110 parts. It is less soluble in alcohol. The solution blackens the skin and other organic matters, the salt being reduced with separation of metallic silver. It melts at 200° and cools to the crystalline solid, usually moulded into sticks, called *lunar caustic*. It dissociates at red heat. It has a metallic taste and acts as a poison.

Silver nitrate is the most used of all the silver salts. It is employed in the laboratory for separating and determining the halogens, in surgery as a cautery, in photography, and in the manufacture of marking-inks.

Silver Phosphates.—There are several silver phosphates, of which the most important are *silver orthophosphate*, Ag_3PO_4, yellow solid; *monohydrogen silver phosphate*, HAg_2PO_4, white crystals; *silver pyrophosphate*, $Ag_4P_2O_7$, white fibrous solid; *silver metaphosphate*, $AgPO_3$, white solid.

Silver Arsenite, Ag_3AsO_3, is a canary-yellow powder.

Silver Arsenate, Ag_3AsO_4, dark-brown crystals.

Several silver vanadates have been prepared.

Silver Carbonate, Ag_2CO_3, is obtained by action of alkali carbonates upon silver solutions. It forms pale-yellow needles which darken in the light and melt at 200°.

Silver Silicates.—Yellow silver silicates of varying composition are formed when silver and silicic oxid or silicates are fused together.

GADOLINIUM.

Symbol Gd. • Atomic weight 156. Valence I.

Gadolinium was discovered by Marignac in 1880, and was named for the Swedish chemist Gadolin, who first described the mineral gadolinite. Its valence is III, and its compounds resemble those of yttrium, lanthanum, and cerium. It is provisionally placed with the cuproids. Among its compounds which have peen prepared are the oxid, hydroxid, halids, double halids, nitrate, sulfate, selenate, vanadate.

GOLD.

Symbol Au. Atomic weight 196. Valence I and III. Specific gravity 19.33. Melting-point 1075°. Specific heat 0.0298.

Occurrence.—Gold occurs free in nature chiefly in quartz-veins and on the bed-rock of streams ancient and modern. It is also found intimately mixed with iron and copper pyrites, with ores of lead and silver, and alloyed with the platinum metals and mercury. It is found in minute quantities in sea-water and in the rocks generally.

Gold is combined in the minerals *petzite* $(AuAg)_2Te$, *sylvanite*, $(AuAg)Te_2$, and *calaverite*, $AuTe_2$.

Gold is widely distributed and has been worked since the earliest times. Many of the European mines are now abandoned because of the discovery of richer fields elsewhere. The chief localities now are Australia, South Africa, Siberia, Alaska, Mexico, Brazil, British Columbia, North Carolina, Georgia, California, Colorado, Oregon, and the States generally west of the Rocky Mountains.

History.—Gold has been known since man began to make history. Its native occurrence, its beauty and luster, its rarity, and its unalterability have caused it in all ages to take the first place among metals—to be indeed, as it has been called, *rex metallorum.* It is mentioned in the Bible and in the earlier writings of all nations. Its names in Hebrew (*zahab*), Greek (*chrusos*), and Sanscrit (*hiranya*) all mean to *glitter* or *shine.* The English name is probably from the Sanscrit *joal*, which means to shine. It was connected with the

sun by the ancients, and the great problem before the alchemists was how to transmute the baser metals into gold.

Preparation.—Native gold is never pure. Its most common companions are silver, copper, and lead. It is separated from copper and lead by cupellation and from silver by parting (see Refining of Silver). Pure gold may be obtained by dissolving in *aqua regia*, evaporating to drive off nitric acid, diluting with water, filtering from silver chlorid, and then precipitating with a reducing agent such as ferrous sulfate or sulfurous oxid.

Gold-mining.—Gold-mining is of two kinds, *placer-mining* and *vein-mining*.

In placer-mining the gold is obtained from the beds of streams or from the sand and gravel of ancient water-courses, where it has been deposited through the agency of the water after having been set free by the disintegration of the rocks. The usual method is to wash the material with powerful streams of water through sluices, in the bottom of which are depressions. The gold, being heavier than the rocks, goes rapidly to the bottom, is retained in the depressions, and is afterwards removed. A method of dry separation of gold from the sand has recently been invented for use in the arid regions where water cannot be had.

Much larger quantities of gold may be taken from quartz-veins. The vein material is crushed to a fine powder under stamps or rollers in the presence of water. The *stamp-mill* consists of a huge mortar in which stamps weighing 600 to 900 pounds are let fall continuously. The pulp is washed through a screen and flows over an amalgamated plate of copper which retains the free gold. It passes then to the concentrating machines, where, by the action of water and gravity, the iron and copper pyrites which contain the so-called combined gold are separated from the other rock material. The gold is taken from the "concentrate" in a chemical way. In the *chlorination process* the gold is dissolved in chlorin and then precipitated with sulfurous oxid. In the *cyanid process* the gold is dissolved out with potassium cyanid and precipitated with metallic zinc.

Physical Properties.—Gold is a yellow lustrous metal of specific gravity 19.33. It melts at 1075° and crystallizes in cubes and dodecahedrons. It is softer than silver and is the most malleable and

ductile of all metals. A single gram of gold may be drawn into a wire 3240 meters (about two miles) long. It may be beaten into leaves one ten-thousandths of a millimeter thick. One gram will gild thirty miles of fine silver wire, the coating having a thickness of only one five-hundredths of a millimeter. Gold-leaf transmits green light.

Gold is obtained in a soluble, colloidal state by reducing a weakly alkaline solution of gold chlorid with formaldehyde. On adding stannous chlorid to a solution of gold chlorid a beautiful red or purple color is produced, due probably to a mixture of colloidal gold and colloidal stannic acid. This is called the *purple of Cassius*, and is used for coloring glass and porcelain.

Chemical Properties.—Gold is the most permanent and unalterable of metals. It does not decompose water, does not tarnish in the atmosphere, is attacked by no single acid, and is but slightly affected by alkalis. It combines directly with chlorin, bromin, and iodin, but not with oxygen, sulfur, or fluorin. It dissolves in chlorin water, aqua regia, potassium cyanid, sulfuric and phosphoric acids in the presence of nascent oxygen $(H_2SO_4+MnO_2 +Au)$, and slightly in alkaline solutions of certain salts, especially those of iron. It is precipitated from its solutions as a dark brown powder by metals and reducing agents.

Tests.—Gold articles are tested by rubbing upon a hard smooth stone and treating the streak with nitric acid. The streak dissolves more or less according to the amount of alloy.

Uses.—On account of its beauty and unalterability gold is the most highly prized of metals, but because of its costliness its use is limited. It is used for coins the world over and is now the almost universal standard of money value. It is employed for jewelry and works of ornament and art, for gilding and gold-plating, for toning photographs, and for coloring ruby glass.

Gold Alloys.—Gold alloys well with most of the true metals, especially silver, copper, lead, tin, mercury, cadmium, and zinc. The copper alloy has a reddish tint, which increases in redness with the amount of copper, but is scarcely noticeable up to 10 per cent The silver alloy increases in whiteness with the amount of silver. Electrum is a pale-yellow alloy of gold with 15 to 25 per cent of silver. It occurs native and was used by the Greeks and Romans in jewelry and coins. The gold coin of the United States, Germany, and most other countries is one tenth copper; that of

England one twelfth copper. Pure gold is worth \$20.67 and coin gold \$18.60 per troy ounce. The gold dollar weighs 25.8 grains.

The composition of art gold has usually been expressed in *carats* or parts in 24. Eighteen-carat gold has 18 parts gold and 6 parts copper. This is the gold most used in jewelry, though lower grades are employed for various purposes.

Gold has a special attraction for mercury and is completely soluble in it. The excess of mercury may be pressed out through chamois leather, leaving the solid-gold amalgam. This is decomposed by heat, the mercury distilling away and leaving the gold. This property is used, as we have already seen, in separating gold from its ores.

Gilding and Gold-plating.—Metals, wood, leather, paper, and earthenware are covered with gold to give beauty and to protect against the air. The gold may be applied in sheets or may be deposited from solution. In the former case gold leaf is used; in the latter the electro-deposition process is usually employed. The object to be gilded is suspended as the cathode in a bath of potassium gold cyanid and the anode is a plate of gold. In gilding porcelain and glassware an organic sulfur gold compound is applied and this is decomposed by heat, leaving the gold upon the surface.

Gold-refining.—The assaying and refining of gold has been explained under silver.

GOLD COMPOUNDS.

Gold is chemically inactive and its compounds are not numerous. They are unstable and are decomposed by heat, leaving pure gold. The valence of gold is I and III. In its aurous compounds it resembles silver, but the auric compounds are the more stable. While gold is a pure metal and positive, it also exhibits acid characteristics, auric hydroxid acting with the more positive metals to form aurates.

The thermal relations are as follows:

(Au,Cl)	= 5,800 cal.	(Au,Br)	= −100 cal.
(Au,I)	= −5,500 cal.	(Au$_2$,O$_3$,Aq.)	= −13,200 cal.
(Au,(OH)$_3$)	= 96,000 cal.	(Au,Cl$_3$)	= 22,800 cal.
(Au,Br$_3$,Aq.)	= 5,100 cal.	(H,Au,Cl$_4$,Aq.)	= 71,300 cal.
(H,Au,Br$_4$,Aq.)	= 41,200 cal.		

Gold Halids.—Gold unites to all the halogens except fluorin, the chlorid being most stable and the iodid least so. There are aurous and auric halids and also haloauric acids or double halids.

Aurous Chlorid, AuCl, is a yellow powder obtained by heating auric-chlorid to 185°. It forms with the alkalies double chlorids or *chloraurites*, as KAuCl₂ or K—Cl=Cl—Au.

Auric Chlorid, $AuCl_3$, is formed by the action of chlorin upon gold at 200°. It is a yellow-brown powder, soluble in water, alcohol, and ether. The aqueous solution contains the acid H_2AuCl_4O, whose silver salt is Ag_2AuCl_3O.

Chlorauric Acid, $HAuCl_4,4H_2O$, separates in long yellow acicular crystals when the solution of gold in aqua regia is slowly evaporated. This is the substance which comes in commerce under the name of "gold chlorid." It colors the skin a dark purple and yields easily to all reducing agents, the gold separating as a brown powder.

This acid forms salts with alkalis, alkaline earths, the ferroids, and the organic bases. *Sodium chloraurate,* $NaAuCl_4,2H_2O$, is the "gold salt" used in toning photographs.

Aurous Bromid, AuBr, is a greenish-yellow micaceous powder obtained by heating bromauric acid to 115°.

Auric Bromid, $AuBr_3$, is a black powder obtained by dissolving gold in hydrobromic acid.

Bromauric Acid, $HAuBr_4,5H_2O$, is obtained as red needle-shaped crystals by the interaction of gold, bromin, and hydrobromic acid. It forms *bromaurates* with the more positive metals.

Aurous Iodid, AuI, is a yellow crystalline powder obtained by action of hydriodic acid upon gold oxid. It is unstable and deposits gold on standing or being heated.

Auric iodid and iodaurates have been described, but need further study.

Aurous Cyanid, Au(CN), is a yellow iridescent powder. It forms with the metals double cyanids or *cyanaurites*, as *potassium cyanaurite*, $KAu(CN)_2$; *ammonium cyanaurite*, $NH_4Au(CN)_2$; *potassium thiocyanaurite*, $KAu(SCN)_2$.

Auric Cyanid, $Au(CN)_3$, has not been separated, but is represented in such compounds as *cyanauric acid*, $HAu(CN)_4,6H_2O$; *potassium cyanaurate*, $2KAu(CN)_4,3H_2O$; *potassium thiocyanaurate*, $KAu(SCN)_4$.

Aurous Oxid, Au_2O, is prepared by treating aurous chlorid with cold potassium hydroxid. It is an unstable violet powder.

Aurous Hydroxid, AuHO, is a violet powder obtained by adding potassium hydroxid to a solution of gold which has been decolorized with sulfurous oxid.

Auric Oxid, Au_2O_3, is an unstable brown powder obtained by heating auric hydroxid above 100°.

Auric Hydroxid, $Au(HO)_3$, is produced as a yellow powder by washing with nitric acid the precipitate obtained by heating gold chlorid solution with excess of magnesia.

Aurates.—Auric oxid and hydroxid yield, when heated with alkalis, salts of the hypothetical auric acid $HAuO_2$. *Potassium aurate,* $KAuO_2,3H_2O$, crystallizes in yellow needles from solution of gold oxid in potassium hydroxid.

Aurous Sulfid, Au_2S, is obtained as a dark precipitate when hydrogen sulfid is passed through boiling solution of gold chlorid. It forms with alkalis *thioaurites,* as KAuS.

Auric Sulfid, Au_2S_3.—When hydrogen sulfid is passed through a cold solution of gold chlorid a brown precipitate falls, which is probably a mixture of aurous and auric sulfids. It dissolves in the alkalis to thiaurites, but with ammonium sulfid yields *ammonium thioaurate,* NH_4AuS_2.

Gold Tellurid, Au_2Te, occurs in the minerals *calaverite* and *sylvanite.*

Gold and the Nitroids.—Gold forms no compound with nitrogen, but unites with phosphorus, arsenic, antimony, and bismuth to form imperfect alloys.

Fulminating Gold.—By action of ammonia upon the oxid, hydroxid, or salts of gold an olive-green powder is obtained, which is caused to explode violently by concussion, friction, or heat. Its probable composition is AuN_2H_4 or $H—N=Au—NH_2$.

Gold Carbid or **Gold Acetylid,** Au_2C_2, is obtained as a yellow explosive powder when acetylene is passed through a solution of gold chlorid to which has been added sodium thiosulfate and ammonia.

Gold Salts.—Gold not being soluble in the acids forms but few salts besides the halids and the halo salts already described. A small number of mixed or double salts have been prepared, such as *sodium aurous sulfite,* $3Na_2SO_3,Au_2SO_3,3H_2O$, and *potassium auric sulfite,* $5K_2SO_3,Au_2(SO_3)_2,5H_2O$.

CHAPTER XXXVIII.

GROUP VII A. THE MANGANOIDS. MANGANESE GROUP.

Manganese 55. Samarium 150.

THIS group contains manganese and probably samarium. Manganese belongs to the first long period and in properties differs much from the elements of Group VII. Indeed it presents the rare phenomenon of possessing properties in common with the three elements which stand about it in the periodic table rather than properties intermediate between them. It forms oxids and ous and ic salts like chromium and iron; manganites and manganates like the chromites and chromates; and peroxid and permanganates like chlorin peroxid and the perchlorates.

Samarium has not been well studied and is placed here provisionally.

MANGANESE.

Symbol Mn. Atomic weight 55. Valence II, III, IV, VI, VII. Specific gravity 8. Melting-point 1900°.

Occurrence.—Manganese does not occur free except in meteorites. In its compounds it is widely distributed, generally associated with other metals, but the oxids are found in rather extensive beds. Its principal ore is *pyrolusite*, MnO_2. Other ores are *braunite*, Mn_2O_3; *hausmannite*, Mn_3O_4; *manganite*, $Mn_2O_2(HO)_2$; *rhodochrosite*, $MnCO_3$; *alabandite*, MnS, and *hauerite*, MnS_2.

History.—Pyrolusite or manganese dioxid has been known from the earliest times. It was confused with magnetic iron ore and called *magnesia*, referring probably to its magnetic properties. In 1740 Pott proved that it contained no iron, and in 1774 Scheele and Bergman showed that it contained a new element. The metal was first isolated by Gahn.

Preparation.—Manganese is separated from its compounds with great difficulty. The oxid is reduced by carbon only at a

bright white heat, a little more easily by aluminum. The fused chlorid is reduced by magnesium or sodium or by electrolysis.

Physical Properties.—Manganese is a steel-gray, brittle, crystalline metal somewhat resembling cast iron and hard enough to scratch glass. It has specific gravity 8, melts at 1900°, and volatilizes in the electric arc.

Chemical Properties.—Pure manganese tarnishes quickly in the air and must be kept under rock oil. When it contains iron it is less easily oxidized. It decomposes cold water slowly, boiling water rapidly, and dissolves readily in dilute acids to form manganous salts.

Manganese Alloys.—Manganese has no commercial use except in its alloys. *Manganese amalgam* is used in electrolytic separation of manganese. *Manganese iron* alloys (spiegeleisen 10 to 20 per cent manganese and ferro-manganese 20 to 80 per cent manganese) are used in the manufacture of Bessemer steel. *Manganese bronze*, an alloy of manganese, copper, and zinc, is used as a substitute for German silver.

MANGANESE COMPOUNDS.

Manganese is basic in its lower and acidic in its higher valences. Its affinities are rather with chromium and iron than with chlorin, since it resembles the last only in the heptoxid and the permanganates. Because of the many valences which it exhibits, there is some confusion in the naming of the compounds. The principal types with the usual names are as follows:

Basic manganese:

Valence II. Manganous compounds: MnO, $MnCl_2$, $MnSO_4$.

Valence III, or pseudotriad, $(Mn_2)^{vi}$, commonly called manganic compounds: Mn_2O_3, $MnCl_3$ or Mn_2Cl_6, $Mn_2(SO_4)_3$.

Acidic manganese:

Valence IV. Manganese dioxid and manganites: MnO_2; K_4MnO_4; K_2MnO_3.

Valence VI. Manganic acid and manganates: MnO_3; H_2MnO_4; K_2MnO_4.

Valence VII. Permanganic acid and permanganates: Mn_2O_7; $HMnO_4$; $KMnO_4$.

Manganese compounds are generally soluble, except the oxids, and are chemically quite active. There are two elemental ions,

$Mn\cdot\cdot$, which is pale red, and $Mn\cdot\cdot\cdot$ or Mn_2^{vi}, which is deep violet; and the compound ions $(MnO_4)''$ green, and $(MnO_4)'$ violet purple; $Mn(CN)_6''''$ blue and $Mn(CN)_6'''$ red.

Thermal equations are as follows:

$(Mn,H_2,O_2) = 163,200$ c. $(Mn,Cl_2) = 112,000$ c. $(Mn,S,Aq.) = 44,400$ c.
$(Mn,S,O_4) = 249,900$ c. $(Mn,C,O_3) = 210,800$ c. $(K,Mn,O_4) = 195,200$ c.
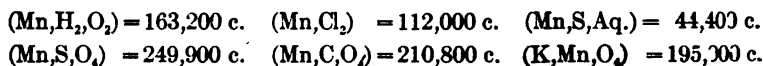
Manganese Halids.—The manganous halids are easily formed and resemble the halids of iron. They are obtained by direct union or by dissolving the oxid, hydroxid, or carbonate in the haloid acids. The tri and tetra halids are unstable and difficult to prepare.

Manganous Fluorid, MnF_2, amethystine crystals.
Manganous Chlorid, $MnCl_2$, $4H_2O$, rose-colored monoclinic crystals.
Manganous Bromid, $MnBr_2$, forms pale-red crystals of $MnBr_2,4H_2O$.
Manganous Iodid, MnI_2 $4H_2O$., colorless deliquescent needles.

Oxids, Hydroxids, and Acids of Manganese.—Of the six oxids of manganese two are basic, three acidic, and one a mixed oxid. They are exhibited in the following table together with the hydrates:

Manganous oxid, MnO.   Manganous hydroxid, MnH_2O_2.
Manganic oxid, Mn_2O_3.   Manganic hydroxid, MnH_3O_3 or
Manganese tetroxid, Mn_3O_4. $Mn_2H_6O_6$.
Manganese dioxid, MnO_2.   Manganous acid, H_4MnO_4 or H_2MnO_3.
Manganese trioxid, MnO_3.   Manganic acid, H_2MnO_4.
Manganese heptoxid, Mn_2O_7.   Permanganic acid, $HMnO_4$.

Manganous Oxid, MnO, is obtained by heating the carbonate or the higher oxids in a stream of hydrogen or by igniting a mixture of anhydrous manganous chlorid and sodium carbonate with a little ammonium chlorid. It is a greenish powder of specific gravity 5.09. It burns in the air to the higher oxids.

Manganous Hydroxid, MnH_2O_2, is obtained as a white precipitate when a solution of a manganous salt is treated with an alkali hydroxid away from the air.   It oxidizes rapidly in the air and dissolves in acids to manganous salts.

Manganic Oxid, Mn_2O_3, occurs as the mineral *braunite* in black square prisms of submetallic luster and specific gravity 4.75. It is prepared by igniting the other oxids in oxygen.   It is a black pow-

der of specific gravity 4.32. It dissolves in hydrochloric acid, evolving chlorin.

Manganic Hydroxid, MnH_3O_3 or $Mn_2H_6O_6$, is obtained as a dark-brown precipitate when ammonia is added to a solution of a manganic salt.

Manganic Metahydroxid, $MnO(HO)$, occurs as the mineral *manganite* in black square pyramids of specific gravity 4.3. It may be prepared by slow oxidation of manganous hydroxid in moist air.

Manganese Tetroxid or **Manganous Manganite,** Mn_3O_4 or Mn_2MnO_4, occurs as the mineral *hausmannite* in red pyramidal crystals of specific gravity 4.85. It is formed when the other oxids are heated in the air and is the most stable of the oxids. When heated with dilute nitric acid it yields manganous nitrate and manganese dioxid, $Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O$. This suggests that it is a manganous salt of orthomanganous acid,

$$Mn{<}^{O}_{O}{>}Mn{<}^{O}_{O}{>}Mn.$$
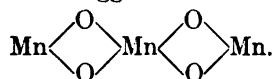
Manganese Dioxid, MnO_2, occurs native as the mineral *pyrolusite* in black rhombic crystals and fibrous masses of metallic luster, and specific gravity 4.82. It may be prepared by gently heating the nitrate. When heated it gives up oxygen and becomes first Mn_2O_3, then Mn_3O_4, and finally at white heat MnO. With hydrochloric acid it yields chlorin. It has been supposed that in this reaction $MnCl_4$ was formed at first, but more careful investigations have shown that the compound H_2MnCl_6 is probably formed and that this breaks down into HCl, $MnCl_2$, and chlorin.

Manganese dioxid is a powerful oxidizing agent and finds extensive use in the manufacture of chlorin, chlorid of lime, oxygen, glass, and porcelain.

Manganous Acid, H_4MnO_4, is formed when an alkaline manganous solution is treated with a strong oxidizing agent such as chlorin, bromin, or a hypochlorite. It makes a brown solution which readily passes to the colloid state. By gentle dehydration it is converted into the meta acid H_2MnO_3. These are weak, unstable acids, which give rise to a series of salts called

Manganites.—These are not simple salts of the acids, but are generally polymanganites. Examples are potassium pentamanganite, $K_2Mn_5O_{11}$, and calcium dimanganite, $CaMn_2O_5$. The latter

is formed by oxidizing a mixture of lime and manganese chlorid, and when treated with hydrochloric acid yields chlorin. These facts are utilized in the recovery of the manganese waste in the manufacture of bleaching-powder.

Manganese Trioxid, MnO_3, is a very unstable, volatile liquid which passes to vapor at 50°. It is obtained by adding a sulfuric acid solution of potassium permanganate to dry sodium carbonate.

Manganic Acid and Manganates.—Manganic acid, H_2MnO_4, is so unstable that it cannot be isolated, but it forms a number of well-defined salts, only, however, with the alkali and alkali-earth metals.

Manganates are obtained by heating together manganese compounds and alkali hydroxids or carbonates with free access of air. The manganates of the alkali metals are soluble, while those of the alkali-earth metals are insoluble in water. The most important of these compounds is *potassium manganate*, K_2MnO_4. It is a green crystalline solid. Its solution is green, but on exposure to the air gradually passes through blue, violet, and purple to red, because of its oxidation to potassium permaganate. On account of this change of color it is called *chameleon mineral*.

Permanganic Oxid, Mn_2O_7, is a heavy, greenish black, mobile liquid which passes at 60° to a violet vapor. It may be obtained by carefully distilling under diminished pressure a mixture of potassium permanganate and moderately dilute sulfuric acid. It explodes with violence when warmed or brought in contact with combustibles.

Permanganic Acid, $HMnO_4$, is a purple substance obtained in solution by dissolving permanganic oxid in cold water or by decomposing barium permanganate with sulfuric acid or by the electrolysis of potassium permanganate. It is quite analogous to perchloric acid, is unstable, and a powerful oxidizer.

Permanganates are obtained by oxidizing the manganates or oxids of manganese in the presence of an alkali. They are all purple red in color, and soluble in water. The most important one is

Potassium Permanganate, $KMnO_4$.—This may be obtained by passing carbon dioxid or chlorin through a solution of potassium manganate:

$$3K_2MnO_4 + 2CO_2 = MnO_2 + 2K_2CO_3 + 2KMnO_4.$$
$$K_2MnO_4 + Cl = KCl + KMnO_4.$$
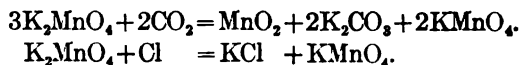
The last equation is written by ions thus:

$$MnO_4'' + Cl = MnO_4' + Cl'.$$
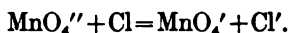
The chlorin takes half the electric charge from the manganate ion. Acids act in the same way, converting the manganate into the permanganate ion.

Potassium permanganate crystallizes from solution in dark purple rhombic needles. It dissolves in 16 parts of water to a deep violet solution. It is a powerful oxidizer and disinfectant, and is much used in laboratories as a reagent. Taken internally it acts as a poison.

The oxidizing action of permanganates is due to the ease with which the permanganate ion is reduced. The action takes place in neutral, alkaline, or acid solutions. In the presence of an acid the colorless manganous ion is formed and five atoms of oxygen are liberated from two molecules of the permanganate:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

In neutral or alkaline solution MnO_2 separates with brown coloration and only three atoms of oxygen are available:

$$2KMnO_4 + H_2O = 2KHO + 2MnO_2 + 3O.$$

A good example of the first action is the oxidation of ferrous to ferric ion in the presence of hydrogen ions:

$$5Fe^{..} + MnO_4' + 8H^. = 5Fe^{...} + Mn^{..} + 4H_2O.$$
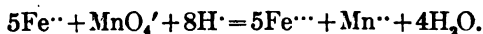
If the permanganate solution is added to the iron solution drop by drop, it is decolorized as long as any ferrous iron is present. The appearance of a persistent color indicates the completion of the oxidation. By using a solution of known strength and measuring the amount used, the amount of ferrous iron in the solution is determined. In the same way the quantities of organic matters in solutions are volumetrically determined.

Other permanganates are those of lithium, sodium, ammonium, barium, calcium, cobalt, magnesium, strontium, zinc, lead, copper,

and lanthanum. Two of these are remarkable for their extreme solubility in water and their extraordinary oxidizing power. Calcium and strontium permanganates dissolve respectively 3.31 parts and 2.9 parts in one part of water at 18°. These strong solutions oxidize organic compounds with almost explosive violence.

Manganous Sulfid, MnS, occurs native as *alabanite* or *manganese blend* in steel-gray cubes and octahedrons of specific gravity 4.04. It may be prepared by heating manganous oxid, carbonate, or sulfate in a stream of hydrogen sulfid. When a manganous salt is treated with ammonium sulfid a flesh-colored precipitate is obtained which is supposed to be MnH_2S_2.

Manganese Disulfid, MnS_2, occurs in nature as *hauerite* in reddish-brown crystals of adamantine luster.

Manganese forms rather well-defined compounds or alloys with phosphorus, arsenic, carbon, silicon, boron, aluminum, tin, and lead.

Manganese Salts.—There are manganous and manganic as well as double and basic salts of nearly all the acids.

Manganous Sulfate, $MnSO_4$, is obtained by heating manganese dioxid with sulfuric acid. It crystallizes with varying quantities of water: at 280°, $MnSO_4,H_2O$, like the native kieserite; at 15°, $MnSO_4,5H_2O$, pink crystals; at 0°, $MnSO_4,7H_2O$, also pink crystals.

Manganese Aluminum Pseudo Alum, $MnAl_2(SO_4)_4,24H_2O$, the mineral *apjohnite.*

Potassium Manganese Alum, $KMn(SO_4)_2,12H_2O$, violet octahedrons.

Ammonium Manganese Alum, $(NH_4)Mn(SO_4)_2,12H_2O$, purple octahedrons.

Manganic Sulfate, $Mn_2(SO_4)_3$, deliquescent powder.

Manganous Nitrate, $Mn(NO_3)_2,6H_2O$, white deliquescent needles.

Manganous Phosphate, $Mn_3(PO_4)_2,7H_2O$, white crystals.

Manganous Carbonate, $MnCO_3$, occurs native as the mineral *rhodochrosite* or manganese spar. It is precipitated from manganous solutions by sodium carbonate as a white powder which turns brown in the air.

Manganese Silicate, $MnSiO_3$, is the mineral *rhodonite.* Manganese is a constituent of many of the complex silicates.

Manganous Borate, MnB_4O_7, is obtained as a brown powder by treating a manganese salt with borax. Added in small quantity to oils and varnishes it acts catalytically to make them dry quickly.

Complex Manganese Compounds.—Manganese forms complex ions with cyanogen similar to those of iron. *Potassium manganocyanid,* $K_4Mn(CN)_6$, is blue, *potassium manganicyanid,* $K_3Mn(CN)_6$, is red.

SAMARIUM.

Symbol Sa.   Atomic weight 150.   Valence III.

Samarium is obtained from orthite and thorite.   It was named by Boisbaudran, who obtained it from samarskite.   It is very rare, its compounds have not been well studied, and its place in the periodic table is not finally established.   The oxid Sa_2O_3 is similar to manganic oxid and dissolves in acids to a yellow solution.   The hydroxid is a white powder insoluble in alkalis.   The salts have an astringent taste.

CHAPTER XXXIX.

GROUP VIII A.—FERROIDS, PALLADINOIDS, AND PLATINOIDS.

THIS group contains three series of elements arranged in three sub-groups. In the series the elements are closely related in atomic weight and properties; in the sub-groups there is the usual group relations and gradation of properties. They may be arranged as follows:

Ferroids: Iron   56   Cobalt   59   Nickel   58.7
Palladinoids: Ruthenium 101.7   Rhodium 103   Palladium 107
Platinoids: Osmium   191   Iridium 193   Platinum 195

These elements are all basic and the basic character increases with the atomic weight in the series. Iron, ruthenium, and osmium are weakly acidic in their higher valences. Nickel, palladium, and platinum ·form no oxygen acids, yet platinum shows a trace of acidic character in the formation of the halo acids and salts such as potassium chloroplatinate, K_2PtCl_6. Cobalt is somewhat anomalous. Its atomic weight is above that of nickel and yet it is less basic and its group affinities are with rhodium and iridium rather than with palladium and platinum. It is probable that further investigation will show that its atomic weight is below that of nickel. In valence there is a gradual progress from Group VII through Group VIII to Group I, as is illustrated by the following compounds:

VI   VII   VI   III   II   I   II
CrO_3 Mn_2O_7 FeO_3 Co_2O_3 NiO Cu_2O ZnO.

These elements occupy the lowest points in the curve of atomic volumes and the highest points in the curve of melting temperatures.

Iron 56.   Cobalt 59.   Nickel 58.7.   ·

Iron, cobalt, and nickel form a series whose physical properties are so similar as to bring them within one group.   Their closest affinities are with chromium and manganese on the one hand and with copper on the other.   They are hard white metals which fuse with difficulty.

IRON.

Symbol Fe.   Atomic weight 56.   Valence II, III, IV, VI.   Specific gravity 7.88.   Melting-point 1600° to 1770°.   Specific heat 0.1138.

Occurrence.—Iron occurs free very sparingly in certain basaltic rocks and in meteorites.   Combined it is one of the most widely distributed and abundant of elements, constituting about one tenth of the surface rocks of the globe.   It is found in almost all soils, rocks, and clays, to which it gives a yellow, brown, or red color.   It is present in nearly all terrestrial waters and is the characteristic constituent of chalybeate mineral waters.   It is found in the chlorophyll of the leaf, in the blood of animals, and in the sun and stars.   Its ores usually lie in beds deposited through the agency of water; sometimes in veins.

The principal ores of iron are *red hematite*, Fe_2O_3, *brown hematite*, $2Fe_2O_3,3H_2O$ or $Fe_4O_3(HO)_6$, *magnetite*, Fe_3O_4, and *siderite*, $FeCO_3$. Other native compounds not used as sources of iron are *iron pyrites*, FeS_2, *copper pyrites*, Cu_2S,Fe_2S_3, and *arsenic pyrites*, FeAsS.

History.—Iron and the method of its separation from its ores have been known from the earliest times.   It was used by the Assyrians, Egyptians, and Greeks, and is mentioned in the books of Moses.   The name is from the Scandinavian *iarn*, German *eisen*, Sanscrit *ayas*.   The symbol is from the Latin name *ferrum*.   It was one of the seven metals of the alchemists and was connected with the planet mars and the god of war.

Preparation.—Pure iron may be obtained—

1. By heating the pure oxid or oxalate in a current of hydrogen.   A soft black powder which takes fire readily in the air and burns to Fe_2O_3.

2. By reducing the ferrous chlorid with hydrogen.   Black, microscopic octahedral crystals.

3. By electrolysis of ferrous sulfate.

4. By reduction of the native ores with carbon.   An impure iron con-

taining more or less carbon, silicon, phosphorus, sulfur, and other impurities.

Physical Properties.—Iron is a hard, white, tenacious, malleable, ductile metal of specific gravity 7.88. It has a typical metallic luster and takes a fine polish. It softens at red heat, may be welded at white heat, melts at 1770°, and is volatile in the electric arc. When cooled from fusion it becomes crypto-crystalline, as may be shown by etching a polished surface with an acid. It may be magnetized, but looses its magnetism as soon as the inducing agent is removed. It absorbs gases at red heat and gives them off on cooling. It conducts heat and electricity, but not so well as copper and silver. It is the strongest and most useful of metals. Its spectrum contains a multitude of lines.

Chemical Properties.—Iron remains unchanged in dry air or oxygen and in oxygen-free water. In moist air or in contact with water it soon becomes coated with iron hydroxid or iron rust, $Fe(OH)_3$. A little acid, even carbonic, and certain salts, especially the haloid salts, promote the oxidation, while alkalis retard it. The rusting begins slowly, but when once started proceeds quite rapidly. This oxidation may be prevented in various ways, as by covering the surface with paint, oil, varnish, or graphite. A layer of black magnetic oxid resists well the action of the air and may be produced by exposing the iron to the action of superheated steam or a strong acid. Iron may also be covered with zinc, tin, or nickel by dipping it in a bath of the molten metal. Thus are obtained *galvanized iron, tin plate,* and *nickeled iron.*

Iron is readily attacked by most dilute acids with evolution of hydrogen, but not by strong acids. It unites directly to the halogens, and when heated burns vividly in oxygen to Fe_2O_3 and Fe_3O_4, and in sulfur vapor to FeS. It decomposes water rapidly at red heat and slowly at 100°.

Iron free and in combination is a peculiarly active catalytic agent. This may be illustrated as follows: Add some potassium iodid starch solution and acetic acid to a dilute solution of hydrogen peroxid. The starch is very slowly blued by the liberated iodin. If now a single drop of a ferrous solution be added, the reaction goes on much more rapidly. It has been suggested that the function of iron in the blood and in the chlorophyll of the leaf is a catalytic one.

The Reduction of Iron Ores.—Iron ores are reduced by the simple metallurgical process of heating them with charcoal, coke or anthracite coal, the reducing agents being both carbon and· carbon monoxid.   The reactions may be represented thus :

$$2Fe_2O_3 + 3C = 3CO_2 + Fe_4 \; ; \quad Fe_2O_3 + 3CO = 3CO_2 + Fe_2.$$
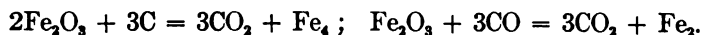
The ores are not pure, but contain much earthy and mineral matter, mostly clay and silica.   These are infusible and prevent the reduction and fusion of the ore.   They are removed by addition of limestone, which acts as a flux (Latin *fluere*, to *flow*); that is, unites with them to form fusible silicates (a kind of coarse glass called slag).

The process is conducted in the blast-furnace, a structure usually about 80 feet high and 25 feet wide, tapering to a smaller diameter above and below, lined with· fire-brick and furnished with inlets below called *tuyeres*, through which a blast of air may be blown.

The ore is first roasted to drive off water and carbon dioxid and to oxidize sulfur, arsenic, and other impurities.   It is then introduced at the top of the furnace along with coke and limestone in proper proportions.

The chemical reactions which go on in the furnace are quite complicated and are not all known.   They are substantially, however, as follows: The carbon below burns to CO_2, is reduced as it passes upward through the hot fire to CO.   This coming in contact with the heated ore reduces it first to ferrous oxid, then to iron (zone of reduction).   The spongy iron as it descends and is more highly heated absorbs carbon, melts, and flows to the bottom of the furnace.   The limestone ·s first converted into lime, then unites with the silica to form the slag, which flows downward and floats on the surface of the molten iron. The slag is drawn off from time to time

Fig. 74.—Iron Furnace.

through a side outlet called the slag-hole and thrown away.   The iron is run off at intervals on a sand floor and is made to flow into channels or moulds which form the *pigs*—bars of iron two or three feet long and about four inches thick.
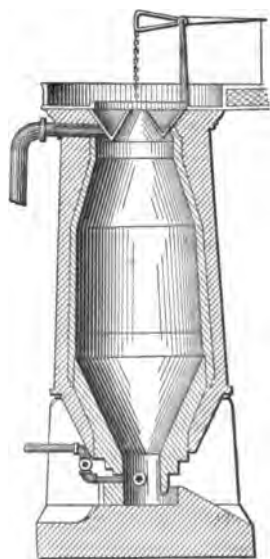
Varieties of Commercial Iron.—The iron as it comes from the furnace, called *pig iron,* is highly charged with carbon, partly com-

bined and partly in small crystals of graphite, and contains other impurities, notably sulfur, phosphorus arsenic, and silica. By refining processes it is converted into many varieties, which may all be roughly classified as *cast iron, wrought iron,* and *steel.*

Cast Iron.—Pig iron is coarsely crystalline, contains some 6 per cent of carbon, and is not suitable for anything but crude castings. By burning out a portion of the carbon and other impurities it is converted into the common cast iron, which still contains from 3 to 5 per cent of carbon. There are two kinds, *white cast iron* and *gray cast iron.*

White cast iron is formed when the melted iron is cooled quickly. It is finely granular and crystalline and contains the carbon in the combined state. It·is hard, brittle, and not malleable, and has specific gravity 7.1. It is pasty at 1200°, does not melt easily to a flowing liquid, and is not suitable for castings. The combined carbon is easily removed by oxidation, and this iron is therefore easily converted into steel and wrought iron.
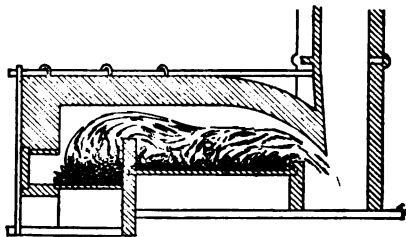
FIG. 75.—REVERBERATORY FURNACE.

White cast iron, which contains 5 to 20 per cent of manganese, is called *spiegeleisen* (German, *looking-glass iron*), and that which contains 20 or more per cent is called *ferro-manganese.* These are much used in the Bessemer steel process.

Gray cast iron is formed when the melted iron is cooled slowly, much of the carbon separating as crystalline graphite. It is not so hard and brittle as white cast iron, fuses more readily, about 1150°, is well adapted for castings, and is not malleable.

Wrought Iron (soft iron, malleable iron) is produced by removing the carbon and other impurities from pig iron or cast iron. This is ordinarily effected by the process called *puddling.* The iron is melted in a reverberatory furnace lined on bottom and sides with

ferric oxid. As the carbon is oxidized the metal boils from the escape of CO_2, and the phosphorus and silica unite with the ferric oxid to form a slag. As the carbon is removed the melting-point of the iron rises and the mass becomes pasty. It is then worked up into balls or *blooms* and removed and worked under hammers or rollers to free it from the slag.

Wrought iron contains less than 0.6 per cent of carbon. It is tough, malleable, ductile, and easily oxidized. It fuses at a higher temperature than either cast iron or steel—1900° to 2100°. It can be rolled hot into thin sheets and welds easily at white heat.

Steel is intermediate between cast and wrought iron and contains from 0.6 to 2.0 per cent of carbon. It is made in three ways:

1. *The Bessemer process.*—Melted cast iron is put into a large oval vessel called a *converter* and a blast of air blown through it until the carbon is all burned out. A quantity of spiegel iron is then added sufficient to furnish carbon enough to convert the whole into steel. By this means any desired amount of carbon may be introduced. The process is rapid and cheap. Six tons of iron may be converted into steel in twenty minutes.

This process is not adapted to iron containing much phosphorus, but a modification called the *basic process* has been used with success. The converter is lined with limestone, which unites with the phosphorus to form calcium phosphate. This is removed and used in the manufacture of fertilizers.

Fig. 76.
BESSEMER CON-
VERTER.

Bessemer steel is hard, strong, crystalline, scarcely malleable, and is called *cast steel.* It is used for rails, axles, cannons, nails, and for all purposes in general where strength, durability, and hardness are desired.

2. *The cementation process.*—Wrought iron is placed in a furnace and covered with broken charcoal and heated to redness until the requisite amount of carbon is absorbed. This is a slow and costly process, requiring several days, but it yields the finer grades of steel used for cutlery, springs, etc.

3. *Siemens-Martin process.*—Wrought iron and iron ore are added to melted pig iron until the whole contains the requisite amount of carbon. The heating lasts ten or twelve hours.

Steel is strong, hard, and tough, may be wrought or cast, welds with difficulty, and melts at from 1200° to 1500°. Its properties are peculiarly modified by the process called tempering. Steel is tempered by cooling it in water or oil or by heating it to various

temperatures after it has been suddenly cooled. When cooled quickly from a high temperature it is very hard and brittle; when cooled slowly it is softer and tough.

The following table shows the composition of average samples of cast iron, steel, and wrought iron.

	Iron.	Carbon.	Silicon.	Phosphorus.	Sulfur.	Manganese.
Cast iron	92.30	4.00	2.00	0.70	0.60	0.40
Steel	98.58	0.90	0.07	0.03	0.02	0.04
Wrought iron .	99.58	0.10	0.05	0.15	0.05	0.07

Alloys of Iron.—Iron forms alloys more or less perfect with many of the metals. With manganese, tungsten, and chromium it fuses in all proportions. The coating of its surface with zinc, nickel, and tin is due to the formation of the alloy. The presence of a small amount of iron in a metal or of a metal in iron often produces a remarkable modification in properties.

Uses.—Iron is the most important and most useful of all metals. Its applications are matters of daily observation and are too numerous to be mentioned.

IRON COMPOUNDS.

Iron resembles manganese in its valences and in the variety of its compounds. While decidedly basic, it shows acidic properties in its higher valences, though not so markedly as manganese. It forms a weak ferric acid, H_2FeO_4, of which there are only a few salts. As a basic element it forms two well-marked series of salts, the ferrous and ferric, besides a few compounds in which the iron is tetravalent.

There are two iron ions, the ferrous, $Fe^{..}$, which is colorless and yields pale-green salts, and the ferric, $Fe^{...}$, which is also nearly colorless and gives red salts. The former is easily oxidized to the latter. There are also several complex ions, the most important of which are FeO_4'', $Fe(CN)_6''''$, and $Fe(CN)_6'''$.

Some of the thermal relations of iron are shown as follows:

(Fe,O)	= 264,700 cal.	(Fe,H₂O₂)	= 136,700 cal.
(Fe,H₃O₃)	= 198,200 cal.	(Fe,Cl₂,Aq.)	= 99,950 cal.
(Fe,Br₂,Aq.)	= 80,800 cal.	(Fe,I,Aq.)	= 46,400 cal.
(Fe,S,Aq.)	= 23,800 cal.	(Fe,S,O₄)	= 235,600 cal.

Iron Halids.—Iron unites directly to the halogens to form ferrous and ferric halids, the affinity becoming less as the atomic weight increases, so that ferric iodid can scarcely be prepared. These compounds are all soluble and form double halids with other metals.

Ferrous Fluorid, FeF_2, green crystals.
Ferric Fluorid, FeF_3, colorless or yellow crystals.

Ferrous Chlorid, $FeCl_2$, is formed by heating iron in chlorin or by dissolving iron in hydrochloric acid away from air and evaporating in hydrogen. It crystallizes in white, lustrous, deliquescent, hexagonal plates. At the ordinary temperature the molecule seems to be Fe_2Cl_4, but the vapor density diminishes as the temperature rises, until at 1400° it corresponds to the formula $FeCl_2$. It forms hydrates and double salts as $FeCl_2,2H_2O$; $FeCl_2,2NH_4Cl$.

Ferric Chlorid, $FeCl_3$, is obtained by heating iron in dry chl rin or by heating ferric oxid in dry HCl or in solution by dissolving iron in hydrochloric acid. It sublimes in reddish-brown or green iridescent scales. It begins to sublime at 100° and boils at 280°. It deliquesces quickly to a dark-brown liquid (called formerly *oleum martis*) and dissolves in water (100 parts in 63.5) with much heat. It dissolves also in alcohol and ether. From concentrated solutions yellow crystals of $FeCl_3,6H_2O$ separate.

The vapor density of ferric chlorid at 440° indicates the formula Fe_2Cl_6, but as the temperature rises dissociation takes place, until at 1000° the formula is $FeCl_3$. It forms numerous double halids such as $FeCl_3,2KCl,H_2O$; $FeCl_3,MgCl_2,H_2O$.

Ferric chlorid is used as a medicine and as a chlorination agent.

Ferrous Ferric Chlorid, $Fe_3Cl_8,18HO$, separates as yellow deliquescent crystals from solution of magnetic iron oxid in hydrochloric acid.

Ferrous Bromid, $FeBr_2$, is obtained by action of bromin or hydrobromic acid upon iron, and separates as $FeBr_26H_2O$ in blue crystals.

Ferric Bromid, $FeBr_3$, is obtained by the action of bromin in excess upon iron or ferrous bromid. It forms dark-red deliquescent crystals.

The commercial iron bromid is a mixture of ferrous and ferric bromid and yields when treated with an alkali carbonate a black precipitate of ferrous ferric hydroxid.

Ferrous Iodid, FeI_2, forms green deliquescent crystals of $FeI_2,5H_2O$.

Ferric Iodid, FeI_3, may be obtained as a brownish-red solution by treating ferrous iodid with iodin.

Hydroferrocyanic Acid or **Cyanferrous Acid, $H_4Fe(CN)_6$.**—Ferrous cyanid, $Fe(CN)_2$, cannot be isolated, because it unites at once with the excess of HCN, by which it is produced to form *hydroferrocyanic acid*. This acid falls as a white crystalline precipitate when a concentrated solution of potassium ferrocyanid is treated with an excess of strong hydrochloric acid. It is tetrabasic and forms a series of characteristic salts called *ferrocyanids* or ferrous cyanids.

Potassium Ferrocyanid or **Potassium Cyanferrite, $K_4Fe(CN)_6$.-$3H_2O$.** This is commonly known as *yellow prussiate of potash*, and is formed by action of potassium cyanid upon iron or iron compounds:

$$6KCN + Fe + 2H_2O = H_2 + 2KHO + K_4Fe(CN)_6.$$
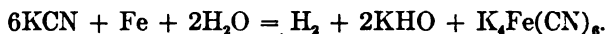
It crystallizes from solution in yellow monoclinic prisms of specific gravity 1.83. It looses its water of crystallization at 100° and at a higher temperature melts with decomposition. One hundred parts of water dissolve 25 parts at 20° and 50 parts at 100°. It is the starting-point for the preparation of numerous cyanogen compounds. It furnishes a test for iron, forming with ferric salts *ferric ferrocyanid*, $Fe_4(FeC_6N_6)_3$, called *Prussian blue*, and for copper whose salts form with it *copper ferrocyanid*, $Cu_2Fe(CN)_6$, known as *Hatchett's brown*. It is decomposed by sulfuric acid with evolution of hydrocyanic acid. With ferrous salts it forms white amorphous *ferrous ferrocyanid*, $Fe_2Fe(CN)_6$, which turns blue on exposure to the air.

Other ferrocyanids are those of sodium, calcium, barium, strontium, bismuth, cobalt, nickel, manganese, and mercury, besides numerous double ferrocyanids.

Hydroferricyanic Acid or **Cyanferric Acid, $H_3Fe(CN)_6$,** is obtained by the action of strong hydrochloric acid upon potassium ferricyanid as an unstable soluble crystalline solid. This acid is tribasic and forms many salts.

Potassium Ferricyanid or **Potassium Cyanferrate, $K_3Fe(CN)_6$,** commonly called *red prussiate of potash*. It is obtained by oxidation of potassium ferrocyanid, as when chlorin is passed through the solution until it no longer gives the Prussian blue reaction:

$$K_4Fe(CN)_6 + Cl = KCl + K_3Fe(CN)_6.$$
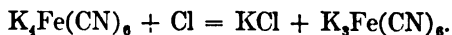
It crystallizes in dark-red monoclinic rhombic prisms of specific gravity 1.8. One hundred parts water dissolve 33 parts at the ordinary temperature and 77 parts at 100°. With ferrous solutions

it gives a precipitate of *ferrous ferricyanid,* $Fe_3''(FeC_6N_6)_2'''$, called *Turnbull's blue,* similar to and possibly identical with Prussian blue.

Nitroprussiates.—Nitroprussic acid, $H_2Fe(CN)_6NO$, is obtained by heating potassium ferrocyanid with dilute nitric acid. On allowing the potassium nitrate to crystallize out, and adding sodium carbonate, the beautiful red crystalline *sodium nitroprussiate,* $Na_2Fe(CN)_6NO,2H_2O$, is obtained. This is used as a test for soluble sulfids, with which it gives an intensely blue color. With hydrogen sulfid no color appears. It may be used for the detection of small quantities of alkalis and alkaline earths by adding a very small quantity to the solution after having passed hydrogen sulfid through it.

Structure of the Ferro and Ferri Cyanids.—The iron and cyanogen in these compounds are so closely united that they do not respond to their usual reagents. They contain the compound negative ions ferrocyanogen, $(Fe''C_6N_6)^{IV}$, tetravalent, and ferricyanogen, $(Fe'''C_6N_6)'''$, trivalent. These are, perhaps, more correctly written $Fe(C_2N_2)_3$ and $Fe(C_2N_2)_3$, the former containing the trivalent radical C_2N_3 and the latter the divalent radical C_2N_2. The structure is not exactly known, but the following suggestion has some probability:

Potassium Ferricyanid:
$$\begin{array}{ccc} K-C=N & & N=C-K \\ | \quad | & & | \quad | \\ N=C & & \\ N=C & > Fe-C=N \\ | \quad | & & \\ K-C=N & & \end{array}$$

Potassium Ferrocyanid:
$$\begin{array}{ccc} K-C-N & & N-C-K \\ \| \quad \| & & \| \quad \| \\ N \quad C-Fe-C \quad N \\ | \quad | & & | \quad | \\ K-C=N & & N=C-K \end{array}$$
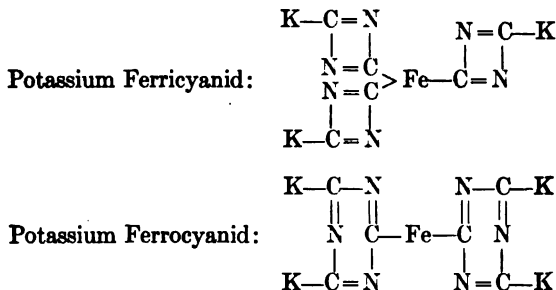
Ferrous Thiocyanate, $Fe(CNS)_2,3H_2O$, is obtained by the action of thiocyanic acid upon iron in pale-green monoclinic crystals.

Ferric Thiocyanate, $Fe(CNS)_3,3H_2O$, is obtained in dark-red cubical crystals by the action of anhydrous ferric sulfate upon potassium thiocyanate under alcohol. It dissolves in water or alcohol to a solution of blood-red color and forms a delicate test for ferric salts and thiocyanates.

Oxids and Hydroxids of Iron.—There are three oxids of iron, *ferrous oxid,* FeO, *ferric oxid,* Fe_2O_3, and *ferrous ferric oxid,* Fe_3O_4 or FeO,Fe_2O_3. The first two are basic and form ferrous and ferric compounds, the last is a mixed compound of the other two, or rather a *ferrous ferrite.* In addition to these there is the hypothetical FeO_3, from which the ferrates are derived. The structure of these oxids

may be represented as follows: Ferrous oxid, $Fe = O$; ferric oxid, $O = Fe—O—Fe = O$, or $O = Fe—Fe = O$; ferrous ferric oxid,

$$Fe\begin{cases} O—Fe = O \\ O—Fe = O \end{cases} ; \quad \text{ferric peroxid, } O = Fe\begin{cases} O \\ O \end{cases}.$$
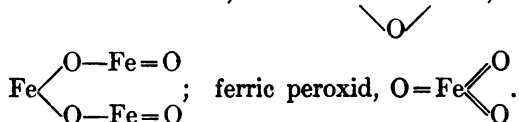
Ferrous Oxid, FeO, is a black powder obtained by reduction of ferric oxid with hydrogen or carbon monoxid or by igniting ferrous oxalate away from the air. It is not pure, but contains some of the metal and of the ferric oxid. It oxidizes quickly in the air and dissolves in acids to form ferrous salts.

Ferrous Hydroxid, FeH_2O_2, is precipitated by alkali hydroxids from ferrous solutions as a white precipitate which soon turns green by oxidation. It oxidizes rapidly in the air, absorbs carbon dioxid with vigor, and is scarcely soluble in water.

Ferric Oxid, Fe_2O_3, occurs native as the mineral *hematite* or *specular iron* in rhombohedrons and scalenohedrons of specific gravity 5.20. It may be prepared by igniting iron compounds, especially the hydroxids, sulfate, and carbonate. It is a dark-red powder insoluble in water and slowly soluble in acids. It is formed in quantities as a waste product of the manufacture of disulfuric acid by roasting ferrous sulfate. It is used as a paint and polishing powder under the name of *rouge* or *colcothar*.

Ferric Hydroxids.—*Ortho ferric hydroxid,* $Fe_2(HO)_6$ or $Fe(HO)_3$, is obtained as voluminous red precipitate when alkali hydroxids are added to ferric solutions. When boiled or gently heated it looses water and becomes monometa ferric hydroxid, $Fe_2O(HO)_4$, which is the chief constituent of *bog iron ore*. On further heating it becomes the dimeta $Fe_2O_2(HO)_2$, which occurs native as *pyrosiderite*. There is also the hydrate $Fe_4O_3(HO)_6$, the native *limonite* or *brown hematite*, which is theoretically obtained by taking six molecules of water from two molecules of the orthohydroxid:

$$2Fe_2(HO)_6 - 6H_2O = Fe_4O_3(HO)_6.$$
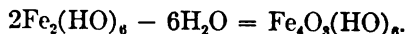
If freshly precipitated ferric hydroxid is dissolved in ferric chlorid or acetate and dialyzed, a red solution of $Fe_2O_2(HO)_2$ is obtained, which is used in medicine under the name of *liquor ferri dialysati*. Upon long standing or upon addition of a few drops of an acid the

hydroxid is precipitated. Ferric hydroxid is the best antidote for arsenical poisoning.

Ocher.—The term *ocher* is applied to various native pigments, which usually consist of ferric oxid or hydroxid mixed with silica and clay. The colors are red, orange, yellow, and brown, with all intermediate shades, and they are called respectively *yellow ocher*, *red ocher*, etc. The color is mainly due to the iron, and hence they are very permanent. They are especially adapted for wood-filling and fresco-work, and are also used in the manufacture of paper, oil-cloth, and linoleum. Special names are *Indian red, orient yellow, raw sienna*, and *Roman ocher*. The color is deepened by burning, as in *burnt sienna* and *burnt Roman ocher*. *Venetian red* is prepared by calcining ferrous sulfate. *Mars red* and *Mars orange* are also artificial preparations.

Ferrous Ferric Oxid or **Magnetic Iron Oxid,** Fe_3O_4, occurs native as the mineral *magnetite* (loadstone) in black octahedrons and dodecahedrons of specific gravity 5.18. It is formed when iron is burned in the air or oxygen. Iron scales from the forge are a mixture of Fe_2O_3 and Fe_3O_4. It is also formed when carbon dioxid or steam is passed over heated iron. It is a hard black brittle solid insoluble in water and slowly soluble in acids. If alkali hydroxids be added to its solution in hydrochloric acid a black magnetic precipitate of $Fe(HO)_2,Fe_2O_3$ falls.

Ferrites.—The ferric hydroxids are basic and do not dissolve in the alkalis to form salts, but still they show weak acidic properties, since certain compounds exist which may be supposed to be derived from them and which are called *ferrites*. Examples are *barium ferrite*, $BaFe_2O_4$, *calcium ferrite*, $CaFe_2O_4$, and *zinc ferrite*, $ZnFe_2O_4$; the last occurs native as the mineral *franklinite*.

Ferrates.—Neither the compound FeO_3 nor its hydroxids have been formed, but there are salts of the hypothetical ferric acid, H_2FeO_4, called *ferrates*.

Potassium Ferrate, K_2FeO_4, formed by heating iron with potassium nitrate or by passing chlorin through a solution of potassium hydroxid containing suspended ferric hydroxid. Potassium hypochlorite is first formed and this oxidizes the iron. The solution has a violet color.

Iron Sulfids.—Iron forms sulfids and hydrosulfids almost exactly analagous to the oxids and hydroxids. They are somewhat more acidic than their oxygen analogues, since the thioferrites are more numerous than the ferrites.

Ferrous Sulfid, FeS, is obtained as a dark-gray metallic solid by fusing together iron and sulfur, or as a black precipitate by action of alkali sulfids upon ferrous and ferric solutions, the latter being first reduced. When moist it oxidizes to ferrous sulfate and when heated in the air it yields ferric oxid and sulfurous oxid. It ·dissolves in dilute acids, evolving hydrogen sulfid, and its most important use is in the manufacture of this gas.

Ferric Sulfid, Fe_2S_3, is a yellow metal-like solid prepared by heating iron and sulfur together in proper proportions.

Thioferrites are derivatives of the hypothetical *meta thioferrous acid*, $HFeS_2$, or FeS(SH). Examples are the alkali thioferrites and the native copper pyrites, which is a *cuprous thioferrite*, $CuFeS_2$, or Cu—S—Fe = S.

Iron Disulfid, FeS_2, occurs native as *iron pyrites*, often called *fool's gold,* in various forms of the cubical system and as *marcasite* in rhombic crystals. It is insoluble in water and not easily attacked by acids, but ·dissolves in hot strong hydrochloric acid, with liberation of sulfur and hydrogen sulfid.

Iron pyrites is often mistaken for gold, but may be easily distinguished as follows: It scratches glass and pulverizes to a greenish-black powder, and when heated gives off sulfur and turns black, while gold is soft and malleable and suffers no change of color.

Ferrous Ferric Sulfid, Fe_3S_4, may be obtained by heating FeS_2. It occurs native with generally a smaller proportion of sulfur, mostly Fe_7S_8, in bronze-yellow hexagonal prisms, magnetic, and of specific gravity 4.4, and often containing a few per cent of nickel.

Selenids and tellurids of iron have been prepared.

Iron Nitrid, $Fe_2N(?)$, is obtained as a gray metallic solid by action of ammonia upon anhydrous iron chlorid.

Iron Phosphid, $Fe_2P(?)$, is obtained by heating iron phosphate with carbon under a layer of sodium chlorid.

Iron Arsenids.—The compound FeAs is obtained by fusing arsenic and iron together. *Löllingite* is $FeAs_2$, *leucopyrite* is Fe_2As_3, and *arsenopyrite* is FeAsS, or Fe = As.
$$\diagdown S \diagup$$

Iron Carbids.—Iron unites to carbon as in white pig iron, but it is in the nature of an alloy rather than a definite compound. Several carbids have been described, however, as follows: Fe_3C, FeC, FeC_2, FeC_3.

Iron Silicids.—Iron alloys with silicon in various proportions, forming the commercial ferrosilicons. At least two definite compounds have been separated: Fe_2Si, crystallizing in prisms, and FeSi, crystallizing in regular tetrahedra.

Iron Salts.—Iron is chemically quite active and forms salts with all the acids. The ferrous salts are generally easily oxidized to the ferric and the latter are the more stable. They are mostly soluble in water and all are soluble in acids. There are basic salts and also many double salts.

Ferrous Perchlorate, $Fe(ClO_4)_2,6H_2O$, light-green deliquescent crystals. The bromate, iodate, and periodate of iron are described.

Ferrous Sulfite, $FeSO_3$, and ferrous thiosulfite, FeS_2O_2, are formed when iron is dissolved in sulfurous acid. The former being less soluble separates out in greenish crystals.

Ferrous Sulfate, $FeSO_4,7H_2O$, is commonly known as *copperas* or *green vitriol.* It is prepared by dissolving iron in dilute sulfuric acid or by the oxidation of iron disulfid in moist air. It occurs native as *melanterite* and in solution in many waters. It has specific gravity 1.9 and is dimorphous, crystallizing in monoclinic and rhombic prisms. It is quite soluble in water, 100 parts dissolving 61 parts at 10°, 150 at 33°, and 333 at 100°. There are several crystalline hydrates, all of which become at 100° $FeSO_4,H_2O$, and at a higher temperature are anhydrous. It easily oxidizes to ferric sulfate and when ignited decomposes, leaving a residue of Fe_2O_3.

Ferric Sulfate, $Fe_2(SO_4)_3$, is obtained as a white powder or in small crystals by oxidizing ferrous sulfate with nitric or sulfuric acid. It is slightly soluble in water and insoluble in strong sulfuric acid. It forms basic and double salts, the most important of the latter being the iron alums which are obtained by treating ferric sulfate with alkali sulfates. Examples are: Potassium iron alum, $KFe(SO_4)_2,12H_2O$; sodium iron alum, $NaFe(SO_4)_2,12H_2O$; ammonium iron alum, $NH_4Fe(SO_4)_2,12H_2O$.

Ferrous Disulfate, FeS_2O_7, is formed by the action of sulfuric acid upon concentrated solution of ferrous sulfate.

Other iron salts belonging here are selenites, selenates, tellurites, tellurates, molybdates, tungstates, and uranates.

Ferrous Nitrate, $Fe(NO_3)_2$, is an unstable, very soluble compound obtained by dissolving iron in cold dilute nitric acid or by treating ferrous sulfate with barium nitrate.

Ferric Nitrate, $Fe(NO_3)_3$, is formed when iron is dissolved in nitric acid. It separates from solution in very deliquescent crystals containing 6 or 9 molecules of water. It is used as a mordant in dyeing and calico-printing.

Ferrous Phosphate, $Fe_3(PO_4)_2,8H_2O$, occurs in monoclinic prisms as the mineral *vivianite*. It is precipitated by ferrous sulfate from sodium phosphate solutions and used as a medicine. When iron is dissolved in phosphoric acid the compound $HFePO_4,H_2O$ is obtained.

Ferric Phosphate, $FePO_4,4H_2O$, is precipitated by sodium phosphate from solutions of ferric chloride as a yellowish powder. It is insoluble in water, soluble in acids except acetic. It is precipitated from its acid solutions by ammonia and the precipitate is not dissolved by acetic acid. In this way it may be separated from the alkali and alkaline earth phosphates. Several basic and hydrous ferric phosphates exist in nature.

There are also phosphites, arsenites, arsenates, and vanadates of iron.

Ferrous Carbonate, $FeCO_3$, occurs native as *siderite* or *spathic iron* ore in rhombohedral crystals. It may be obtained by precipitating ferrous sulfate solution with sodium carbonate as a white powder, soon turning brown from oxidation. It dissolves in water and water containing carbon dioxid and is the characteristic constituent of chalybeate waters.

Ferric carbonate cannot be isolated because of its instability. If sodium carbonate be added to a ferric solution, ferric hydroxide separates and carbon dioxid is evolved:

$$2FeCl_3 + 3Na_2CO_3 + 3H_2O = 6NaCl + 2Fe(HO)_3 + 3CO_2$$
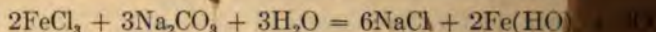
Iron Carbonyl.—Finely divided iron absorbs carbon monoxid, giving rise to *iron pentacarbonyl*, $Fe(CO)_5$, a pale-yellow liquid of specific gravity 1.47, boiling-point 103°, and freezing-point −21°. Other compounds are $Fe(CO)_4$ and $Fe_2(CO)_7$, the latter being a crystalline solid. The formula suggested for the pentacarbonyl is $CO < \frac{CO-CO}{CO-CO} > Fe$.

Iron Silicates.—Ferrous and ferric ortho and meta silicates are constituents of nearly all silicious rocks except quartz. Ferric iron replaces aluminum and ferrous iron the alkalis and alkaline earth metals to form complex double silicates.

Iron Borates.—Ferric borate, $Fe_2(BO_3)_2,3H_2O$, has been found in nature. Basic borates are formed by the action of alkali borates upon ferric salts. There are also double borates of iron and the alkali metals.

COBALT.

Symbol Co. Atomic weight 59. Valence II and III. Specific gravity 8.9. Melting-point 1200°.

Occurrence.—Cobalt is found free in meteorites and in the atmosphere of the sun. Combined it is rare and not widely distributed.

Its principal native compounds are *smaltite*, $CoAs_2$, *cobaltite* (cobalt glance), CoAsS, and *erythrite* (cobalt bloom), $Co_3As_2O_8,8H_2O$. In all these a portion of the cobalt is often replaced by iron or nickel.

History.—The name cobalt is from the German *kobold, an evil spirit*, and was given to certain ores from which the miner could not obtain the expected metal. The same ores were used in the preparation of *smalt*, a potassium cobalt glass of fine blue color. The metal was first prepared by Brandt in 1733, and was more carefully studied by Bergman in 1780.

Preparation.—Cobalt is obtained by reducing the oxid or chlorid with hydrogen or carbon or by igniting the oxalate under powdered glass.

Physical Properties.—Cobalt is iron-white with a tinge of red, has metallic luster, takes a fine polish, is harder than iron, and has specific gravity 8.7 to 8.9. At red heat it is malleable and ductile and at 1200° absorbs carbon and melts.

Chemical Properties.—Cobalt tarnishes slightly in moist air. When finely divided, as when it is obtained by reducing the oxid with hydrogen, it oxidizes rapidly, often with incandescence. It burns when heated in the air to Co_3O_4, and decomposes steam, becoming CoO. It dissolves slowly in most acids, evolving hydrogen; rapidly in nitric acid, liberating oxids of nitrogen.

Uses.—Cobalt has limited application in the arts. The oxids are used for coloring glass and porcelain blue.

COBALT COMPOUNDS.

Cobalt yields two principal elementary ions Co·· and Co··· or (Co_2)···· which give rise to cobaltous and cobaltic compounds, the former being most abundant. It also forms a number of complex ions. Hydrous cobaltous salts are pink, while without water they are blue. Thermal equations are as follows: (Co,H_2,O_2) = 131,800 cal., (Co,Cl_2) = 76,500 cal., $(Co,S,Aq.)$ = 19,700 cal., $(Co,SO_4,Aq.)$ = 230,500 cal.

Cobalt Halids.—The cobalt halids are formed by direct union of the elements or by dissolving the oxid or carbonate in the haloid acids. They crystallize with $6H_2O$, which they gradually lose when heated. At 120° to 130° they are anhydrous.

Cobalt Fluorid, $CoF_2,2H_2O$, forms rose-colored crystals.

Cobalt Chlorid, $CoCl_2$, a blue crystalline solid, dissolves in

alcohol to a blue solution, which turns red upon It crystallizes from water in red monoclinic prisms of $CoCl_2$ writing be made upon white or pink paper with the aqueous it is invisible. If the paper be heated, the letters appear in bright blue, and on exposure to moist air they disappear again. Such a liquid is called *sympathetic ink*.

Cobalt Bromid, $CoBr_2$, is a green deliquescent solid which forms several crystalline hydrates, the most important of which is $CoBr_2,6H_2O$.

Cobalt Iodid, CoI_2, is a black solid which forms green crystals of $CoI_2,2H_2O$ and red crystals of $CoI_2,6H_2O$.

Cobalt Cyanid, $Co(CN)_2$, is a reddish so.id which crystallizes with $2H_2O$.

Cobalto and Cobalti Cyanids.—These compounds are exactly analogous to the ferro and ferri cyanids. The cobalto cyanids readily oxidize to the cobalti forms, and hence are not easily prepared. Examples are: Potassium cobaltocyanid, $K_4Co(CN)_6$; potassium cobalticyanid, $K_3Co(CN)_6$.

Cobalt Oxids.—The two oxids, cobaltous, CoO, and cobaltic, Co_2O_3, are both basic and form hydroxids; the third oxid, Co_3O_4, is a mixed compound of the other two, or a cobaltous cobaltite, Co_2CoO_4.

Cobaltous Oxid, CoO, is obtained by reducing the higher oxids with hydrogen or by heating oxids or carbonate away from the air. It is a gray powder insoluble in water. *Zaffre* is an impure cobaltous oxid obtained from cobalt ores. It generally contains arsenic and nickel.

Cobaltous Hydroxid, $Co(HO)_2$, is precipitated from hot cobaltous solutions by alkali hydroxids. It is a rose-red powder which readily oxidizes to cobaltic hydroxid and dissolves in acids to form cobaltous salts.

Cobaltic Oxid, Co_2O_3, is obtained as a brown powder by igniting the nitrate.

Cobaltic Hydroxid, $Co(HO)_3$, is obtained by oxidizing the cobaltous hydroxid or by treating a cobaltic salt with an alkali hypochlorite. It dissolves in acids to form unstable cobaltic salts.

Cobalt Tetroxid, Co_3O_4, is a black powder obtained by heating the oxid, hydroxid, or nitrate with free access of the air. It is insoluble in water and acids except sulfuric.

Cobaltates.—Cobalt dioxid, CoO_2, and its corresponding acid, H_2CoO_3, have not been isolated, but a few salts of the acid are known. An example is *magnesium cobaltite*, $MgCoO_3$.

Cobaltous Sulfid, CoS, falls as a black hydrous precipitate when cobaltous salts are treated with ammonium sulfid. It dissolves in the acids

except acetic. The anhydrous compound is obtained as a bronze color-less solid by heating cobaltous oxid with sulfur.

Other cobalt sulfids are Co_3S_4 and CoS_2, obtained by heating cobaltous sulfid w.th sulfur. The former occurs ñative as *linnæite*.

Cobalt with Nitrogen, Phosphorus, and Arsenic.—Cobalt does not unite with nitrogen and forms a rather loose compound with phosphorus. With arsenic the union is more definite. Native compounds are *skut-terrudite*, $CoAs_3$; *smaltite*, $CoAs_2$, and *cobaltite*, CoAsS.

Cobalt Carbid.—Heated cobalt absorbs carbon like iron, but definite compounds have not been isolated.

Cobalt Silicid, Co_2Si, is obtained by fusing the elements together.

Cobalt Salts.—Cobalt forms salts similar to those of iron. They are obtained by dissolving the oxid or carbonate in the acids. The solutions are usually pink, but when concentrated or heated they are blue. The change of color is due to the change in degree of hydration. Cobaltic salts are unstable.

Cobaltous Sulfate, $CoSO_4,7H_2O$, crystallizes in red prisms of specific gravity 1.92. It has a metallic, astringent taste, dissolves in water, and looses its water of crystallization easily when heated.

Cobaltous Nitrate, $Co(NO_3)_2,6H_2O$, forms red crystals.

Cobalt Phosphates.—Numerous phosphates of cobalt, ortho, meta, and pyro, have been prepared. They are generally insoluble crystalline salts, single or double, with more or less water of crystallization.

Cobalt Arsenates are similar to the phosphates. Zaffer contains an impure basic arsenate, $CoO(AsO_4)_2$.

Cobaltous Carbonate, $CoCO_3$, is a red finely crystalline powder obtained by heating together cobaltous chlorid and hydrogen sodium carbonate. The hydrous salt, $CoCO_3,6H_2O$, is prepared by decomposing cobaltous nitrate with sodium carbonate.

Cobalt Silicates.—Cobalt forms double silicates with the alkalis in the form of the blue glass called *smalt*, and is much used in the manufacture of art glass and porcelain. Powdered smalt is used as a pigment. *Cobalt blue* (Thénard's blue) contains a potassium or sodium cobalt aluminate.

Ammonio-cobalt Salts.—Cobalt forms two series of complex compounds with ammonia and acid radicals. The *ammonio cobaltous* compounds are formed by dissolving cobaltous salts in strong ammonia away from the air. Only a few have been prepared, all of the type $Co(NH_3)_6Cl_2$, in which the chlorin may be replaced by acid radicals.

The *ammonio cobaltic* compounds are more numerous and more stable. They are obtained by treating cobaltic compounds with ammonia in the presence of the air or other oxidizing agents. Their structure is not cer-

tainly known. They contain trivalent radicals in which the cobalt atom is combined with ammonia, as $[Co(NH_3)_n]'''$, in which n is equal to 3, 4, 5, or 6. They are hence of four types and the chlorids may be taken as illustrations. The following formulas are suggestions of probability and do not represent ascertained structure:

First type—Triammonio cobaltic chlorid (Dichrocobaltic chlorid):

$$Co(NH_3)_3Cl_3;\quad Co(NH_3—Cl)_3.$$

Second type—Tetrammonio cobaltic chlorid (Praseocobaltic chlorid):

$$Co(NH_3)_4ClCl_2;\quad Co\diagup{NH_3—NH_3—Cl}\diagdown{(NH_3—Cl)_2}\ .$$
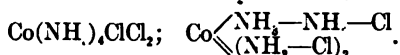
Third type—Pentammonio cobaltic chlorid (Roseocobaltic chlorid hydrous and Purpureocobaltic chlorid anhydrous):

$$Co(NH_3)_5Cl_2Cl_3;\quad Co\diagup{(NH_3—NH_3—Cl)_2}\diagdown{NH_3—Cl}\ .$$
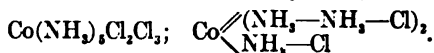
Fourth type—Hexammonio cobaltic chlorid (Luteocobaltic chlorid):

$$Co(NH_3)_6Cl_3;\quad Co(NH_3—NH_3—Cl)_3.$$
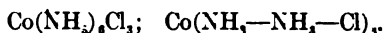
The chlorin in these compounds may be replaced by (HO), (NO_3), or any negative acid ion, as $(SO_4)''$, $(NO_3)'$, etc. Again in types 2 and 3 the radical connected to the cobalt by $2(NH_3)$ dissociates more easily than the others, so that two or more classes of derivatives may be formed.

NICKEL.

Symbol Ni. Atomic weight 58.7. Valence II and III. Specific gravity 8.9. Melting-point 1500°. Specific heat 0.109.

Occurrence.—Nickel occurs free in meteorites and in the atmosphere of the sun. The principal native ores are *niccolite* (kupfer nickel), NiAs; *nickel glance*, NiAsS; *nickel blende*, NiS. Nickel is a constituent of many ores and is nearly always associated with cobalt, frequently with iron, arsenic, antimony, and bismuth.

History.—The name *kupfernickel* (false copper) was applied to the native nickel arsenid because it resembled copper ore, but yielded no copper. The last part of the name was given to the element by Cronstedt, who discovered the metal in 1751.

Preparation.—Nickel is obtained as a gray powder by reducing the oxid in hydrogen, as a solid mass by igniting the oxalate or reducing the oxid with carbon.

Physical Properties.—Nickel is a silver-white metal, malleable and ductile, takes a fine polish, has about the hardness, melting-point, and magnetic properties of iron, and specific gravity 8.9.

Chemical Properties.—Nickel tarnishes slowly in moist air, but in fine powder takes fire easily and burns to NiO. It absorbs carbon monoxid to form nickel carbonyl, $Ni(CO)_4$, a liquid which boils at 43° and is solid at − 25°. It dissolves in dilute hydrochloric and sulfuric acids, with evolution of hydrogen. With strong sulfuric acid SO_2 is given off, and with nitric acid NO. It decomposes steam slowly at red heat. When dipped in strong nitric acid it becomes *passive* like iron. The soluble nickel compounds are quite poisonous.

Nickel Alloys.—Nickel forms alloys with other metals. Those of most importance are German silver and nickel coin.

German silver is an alloy of nickel, copper, and zinc in varying proportions, generally about—copper 5, nickel 2, and zinc 2. The addition of 2 per cent of iron makes the alloy whiter, harder, and more brittle.

Nickel coin of the United States, Germany, and Belgium contains one part of nickel to three parts of copper.

Nickel-plating.—Nickel is much used in electroplating other metals, especially iron and steel. It protects the iron well, is hard and durable, and makes a beautiful polished surface.

NICKEL COMPOUNDS.

Nickel compounds are similar to those of iron and cobalt. Nickel has, however, no trace of negative quality and forms neither acid nor nickelate. The elementary ion is $Ni^{..}$, green. There are a few nickelic compounds, but they are easily reduced. The complex ions are similar to those of cobalt.

Nickel Halids.—The nickel halids may be obtained anhydrous or hydrous.

Nickel Fluorid, $NiF_2,3H_2O$, blue-green crystals.

Nickel Chlorid, $NiCl_2$, prepared by direct union; golden-yellow scales. From solution it forms yellow crystals of $NiCl_2,6H_2O$.

Nickel Bromid, $NiBr_2$, yellow scales; $NiBr_2,3H_2O$, green crystals.

Nickel Iodid, NiI_2, black lustrous scales; $NiI_2,6H_2O$, green crystals.

Nickel Cyanid, $Ni(CN)_2$, green solid; forms several hydrates.

Nickel Ferrocyanid, $Ni_2Fe(CN)_6$, and nickel ferricyanid, $Ni_3[Fe(CN)_6]_2$; and numerous double and mixed ferro and ferricyanids have been prepared.

Nickel Oxid, NiO, is obtained as a green powder by igniting the hydroxid, carbonate, or nitrate. It does not oxidize further in the air and

is easily reduced by carbon or hydrogen. It dissolves in acids to form nickelous salts.

Nickel Hydroxid, $Ni(HO)_2$, is precipitated as a green powder from nickelous solutions by alkali hydroxids. It dissolves in ammonia to a blue solution.

Nickelic Oxid, Ni_2O_3, is obtained as a black powder by gently igniting the nitrate or carbonate. When dissolved in acids it generally forms nickelous salts.

Nickelic Hydroxid, $Ni(HO)_3$, is obtained as a black solid by passing chlorin through water containing nickelous hydroxid or by treating a nickelous solution with sodium hypobromite.

Nickel Tetroxid, Ni_3O_4, is a gray metallic mass obtained by heating nickel chlorid to 400°.

Nickel Sulfids.—Nickel sulfid, NiS, occurs as *millerite* or *nickel blende*. It may be prepared by heating nickel and sulfur together. Several double sulfids of nickel and other metals occur in nature and *nickel disulfid*, NiS_2, may be prepared.

Nickel Phosphid, Ni_2P, and **Nickel Arsenid,** NiAs, are formed when the elements are fused together. Several arsenids occur native.

Nickel Silicid, Ni_2Si, has been prepared.

Nickel Salts.—Only nickelous salts can usually be obtained because of the instability of nickelic compounds. They are yellow when anhydrous and green when hydrous. They are closely analogous to the cobaltous salts and need not be described here in detail. A few only will be mentioned.

Nickel Sulfate, $NiSO_4, 7H_2O$, forms green crystals which loose their water at 300°. It forms various double salts, the most important of which is nickel ammonium sulfate, $Ni(NH_4)_2(SO)_2, 6H_2O$, used in nickel-plating.

Nickel Nitrate, $Ni(NO_3)_2$, green monoclinic crystals.

Nickel phosphates, arsenates, and silicates are insoluble in water and occur in native minerals.

Nickel Carbonate, $NiCO_3$, is a very unstable pale-green crystalline powder obtained by heating calcium carbonate with nickel chlorid solution.

Ammonio Nickel Compounds.—Nickel forms a few compounds with ammonia, as $Ni(NH_3)_6Cl_2$, similar to the ammonio cobaltous compounds.

THE PALLADINOIDS. PALLADIUM SERIES.

Ruthenium 101.7.   Rhodium 103.   Palladium 107.

These are the transition elements of the second long series and present the usual gradation in properties. They are rare substances, and the last is the most important. They are all white metals with high melting-points and specific gravity about 12. They are basic elements, but ruthenium is weakly acidic in its higher valence.

RUTHENIUM.

Symbol Ru.   Atomic weight 101.7.   Valence II, III, IV, VI, VII, and VIII.   Specific gravity 12.26.   Melting-point about 2000°.

Occurrence.—Ruthenium is generally a constituent of platinum ores and osmiridium, and is also found as the sulfid in the mineral *laurite* Ru_2S_2.

History.—In 1828 Osann announced that he had discovered three new metals in a Russian platinum ore, one of which he called *ruthenium*, from *Ruthenia*, a name of Russia. In 1845 Claus showed that Osann's ruthenium oxid consisted mainly of other oxids, but still contained a small amount of a new metal, and retained for it the name *ruthenium*.

Preparation.—Ruthenium is obtained from the osmiridium which contains it by a process too complicated to be here described. It may be prepared by reducing the oxid with carbon or hydrogen.

Properties.—Ruthenium is hard, white, lustrous, and brittle and has specific gravity 12.26. It is one of the most difficultly fusible of all metals, melting about 2000°. It is unchanged in the air, but oxidizes slowly when melted. It is not attacked by acids, but when finely divided unites to chlorin and dissolves in hot aqua regia and in boiling alkali hydroxids. It alloys with tin, lead, zinc, gold, silver, and with all the platinum metals.

RUTHENIUM COMPOUNDS.

Ruthenium forms numerous compounds exhibiting valences from II to VIII. It is usually basic, but forms salts of the hypothetical ruthenic acid, H_2RuO_4, as well as haloruthenates like K_2RuCl_6.

Ruthenium Halids.—Ruthenium forms three series of halids with valences II, III, and IV, of which the chlorids may be taken as examples.

Ruthenium dichlorid, $RuCl_2$, a black insoluble powder.

Ruthenium trichlorid, $RuCl_3$ or Ru_2Cl_6, yellow crystals.

Ruthenium tetrachlorid, $RuCl_4$, found mainly in combination with other chlorids as chlororuthenates, as $2KCl,RuCl_4$ or K_2RuCl_6.

Ruthenium Oxids.—Ruthenium forms no less than six oxids: RuO, Ru_2O_3, RuO_2, RuO_3, Ru_2O_7, and RuO_4. Two of these, RuO_3 and Ru_2O_7, have not been isolated, but are represented in various compounds. Ruthenium tetroxid is a volatile, crystalline solid which melts at 40°, boils at 100°, and yields a vapor which is very irritating to the eyes and mucous membrane.

Ruthenium Hydroxids.—The oxids, Ru_2O_3 and RuO_2, yield the hydroxids, $Ru_2(HO)_6$ or $Ru(HO)_3$ and $Ru(HO)_4$.

Ruthenium Acids and Ruthenates.—No acids have been isolated. The oxids, RuO_3 and Ru_2O_7, form the theoretical ruthenic acid, H_2RuO_4, and perruthenic acid, $HRuO_4$, whose salts are called *ruthenates* and *perruthenates*.

Ruthenium forms ammonio, nitroso, and cyano compounds similar to those of cobalt and platinum.

RHODIUM.

Symbol Rh. Atomic weight 103. Valence II, III, and IV. Specific gravity 12.1. Melting-point about 1800°.

Occurrence and History.—Rhodium occurs in small quantities in platinum ores and in some native golds. It was discovered by Wallaston in 1803. The name is from the Greek and means a *rose*, referring to the rose-red color of many rhodium salts.

Preparation.—Rhodium is prepared from the platinum residues by first converting it into ammonio rhodium chlorid and then reducing this by heating it with sulfur in a carbon crucible.

Properties.—Rhodium is a silver-white, malleable, ductile metal of specific gravity 12.1. It fuses with more difficulty than platinum, about 1800°. It is insoluble in the acids and unchanged in the air. In fine powder it is an active catalytic agent. It forms alloys with platinum, gold, bismuth, lead, etc. If the per cent of rhodium is small, the alloy dissolves in aqua regia.

Rhodium is the most costly of the noble metals, being worth about five times as much as gold. Neither rhodium nor its compounds has any commercial importance.

RHODIUM COMPOUNDS.

The most common valence of rhodium is III, but it also acts with valences II and IV. It shows a trace of negative character in the formation of halorhodates. Its compounds are similar to those of iridium and platinum.

PALLADIUM.

Symbol Pd. Atomic weight 106. Valence II, III, and IV. Specific gravity 11.8. Melting-point 1500°.

Occurrence.—Palladium occurs in the ores of platinum, silver, and selenium, and in native gold from Brazil.

History.—Palladium was discovered by Wallaston in 1803. It was named for the new planet Pallas, which was discovered by Olbers in 1802.

Preparation.—Palladium is separated from the platinum residues as cyanid or iodid. It is most easily obtained from Brazilian gold by melting with silver, dissolving in nitric acid, and displacing the palladium with zinc.

Properties.—Palladium has the color, luster, and appearance of platinum, but takes a finer polish. It is malleable and ductile and is the most easily fusible of the platinum metals. It melts at 1500° and at a higher temperature yields a green vapor. It is rather easily scluble in acids and in a finely divided state is highly catalytic.

Palladium is used for the graduated surfaces of physical instruments and for coating silver articles, especially mirrors, because it retains its polish and does not tarnish.

Palladium Alloys.—Palladium forms alloys with gold, silver, copper, mercury, nickel, antimony, arsenic, and the platinum metals.

Palladium Hydrid.—Palladium absorbs at various temperatures from 400 to 900 times its volume of hydrogen, forming an alloy or a loose compound from which the hydrogen is expelled by heat. The alloy has a metallic appearance and is lighter than palladium, having a specific gravity 11.06. If a piece of palladium be heated in a gas flame it becomes blackened with carbon, the palladium decomposing the hydrocarbons and absorbing the hydrogen.

Illustration.—Pass hydrogen for half an hour through a U-tube containing spongy palladium and immersed in boiling water. Allow the tube to cool still filled with hydrogen and connect with an inverted water-filled cylinder by a delivery-tube reaching the top of the cylinder. On heating the U-tube over the free flame the hydrogen is expelled into the cylinder, and on allowing it to cool the gas is absorbed again.

PALLADIUM COMPOUNDS.

Palladium acts with valences II and III, forming palladous and palladic compounds, the former of which are the most stable. It is basic, but shows a trace of acidic character in the halopalladates.

Palladium Halids.—Palladium unites rather readily with the halogens, forming compounds such as *palladous chlorid*, $PdCl_2,2H_2O$, reddish-brown crystals, and *valladic chlorid*, $PdCl_4$, a brown solution.

Halopalladates.—Palladium forms halosalts such as *potassium chloropalladate*, K_2PdCl_4, dichroic prisms, and *ammonium chloropalladate*, $(NH_4)_2PdCl_4$, bronze-yellow crystals.

Ammonio Palladium Compounds correspond to those of cobalt and platinum. Examples are: *Palladammonia hydroxid*, $Pd(NH_3)_2(HO)_2$, yellow crystals, and *palladammonia cyanid*, $Pd(NH_3)_2(CN)_2$, pearly crystals.

Palladium Oxids and Hydroxids.—Palladium forms three oxids:

Hypopalladous oxid, Pd_2O, a black powder obtained by heating PdO.

Palladous oxid, PdO, black powder obtained by heating the nitrate.

Palladic oxid, PdO_2, a black powder obtained by precipitating palladic chlorid or potassium chloropalladate with KHO.

Palladium does not form hydroxids. Several sulfur compounds are described.

Palladium Salts are unstable and not numerous.

THE PLATINOIDS. PLATINUM SERIES.

Osmium 191.   Iridium 193.   Platinum 194.8.

Osmium, iridium, and platinum are the transition elements of the third long series. Osmium is the heaviest and most difficultly fusible of all the elements, and platinum is the most inactive, permanent, and durable of the metals except gold. They are basic, but osmium, like iron and ruthenium, forms acids and iridium and platinum form halo salts.

OSMIUM.

Symbol Os.   Atomic weight 191.   Valence II, III, IV, VI, VIII. Specific gravity 22.48.   Melting-point about 2500°.

Occurrence.—Osmium is always a constituent of platinum ores, and is also found in osmiridium.

History.—Osmium was discovered by Tennant in 1804. Its name is from the Greek *osme, smell*, referring to the peculiar odor of the tetroxid.

Preparation.—Osmium is separated from the metals with which it is associated as the volatile tetroxid. This is converted into the amalgam or sulfid and then the metal is liberated by heat.

Properties.—Osmium is a bluish, shining metal, harder than glass and infusible in the oxyhydrogen flame. It crystallizes in cubes or rhombohedrons and is the heaviest of solids, its specific gravity being 22.48. It burns in the air to osmium tetroxid, which has a peculiar penetrating odor and is very injurious to the eyes. It alloys with metals, notably with iridium. It is used in pointing gold pens and as bearings for compass-needles.

OSMIUM COMPOUNDS.

Osmium is quite active, and like the other platinum metals has a ten-dency to form double and complex compounds with the halogens and ammonia. It has no less than five valences, as is indicated by its oxids and their derivatives.

Osmium Oxids.—Osmium forms five oxids, OsO, Os_2O_3, OsO_2, OsO_3, OsO_4. The first three are black powders, the fourth is represented in the salts of osmic acid, and the fifth is a soft white crystalline solid which sublimes at a low temperature and boils about 100° , yielding a colorless, very poisonous vapor. This last is easily reduced to the lower oxids and dissolves in water to the solution known as osmic acid, which is used for hardening animal sections in histological operations. The hydroxid $Os(HO)_4$ is formed when the solution of the tetroxid is mixed with alcohol or a reducing agent.

Osmic Acid, H_2OsO_4, has not been obtained free. It is no doubt formed by reduction when osmium tetroxid, OsO_4, is dissolved in water.

Other Osmium Compounds. — Osmium compounds in general re-semble those of ruthenium. The following are mentioned for the sake of illustration:

Osmium dichlorid, $OsCl_2$, green deliquescent needles.

Osmium trichlorid, $OsCl_3$, purple amorphous solid.

Potassium chlorosmite, $K_3OsCl_6,3H_2O$, dark-red crystals.

Osmium tetrachlorid, $OsCl_4$, a red sublimate.

Potassium chlorosmate, K_2OsCl_6, dark-brown octahedrons.

Cyanosmous acid, $H_4Os(CN)_6$, colorless hexagonal prisms.

Osmium tetrasulfid, OsS_4, brown powder..

IRIDIUM.

Symbol Ir. Atomic weight 193. Valence II and IV. Specific grav-ity 22.42. Melting-point about 2200°.

Occurrence.—Iridium occurs generally in the platinum ores and some-times in such quantity as to give them the names *platiniridium* and *os-miridium.*

History.—Iridium was discovered at the same time with osmium by Tennant in 1804. The name is from *iris, the rainbow,* referring to the varying colors of its salts.

Preparation.—Iridium is obtained by igniting ammonium chloriri-date, $(NH_4)_2IrCl_6$, which is obtained from osmiridium or the platinum residues by processes too complicated to be here described.

Properties.—Iridium is a hard, white, lustrous metal resembling steel. It is malleable at red heat, but melts only in the oxyhydrogen flame and in the electric furnace at about 2200°. It is brittle and exceedingly

hard and has specific gravity 22.42. When finely divided it is powerfully catalytic. It may be obtained in fine powder by exposing the alcoholic solution of the sulfate to sunlight, and as sponge by igniting ammonium chloriridate. Massive it does not tarnish in the air and is not attacked by acids, but in powder it oxidizes readily and dissolves in aqua regia.

Iridium Alloys.—Iridium forms numerous alloys. The native osmiridium has already been mentioned. An alloy of platinum and iridium, 10 to 1, is used for various techincal purposes, notably for making the standard weights and measures of the metric system which are kept in the government archives at Paris.

IRIDIUM COMPOUNDS.

Iridium compounds are analagous to those of nickel and rhodium. The element is mainly basic, but forms halo salts. The more common valences are III and IV.

Iridous oxid, Ir_2O_3, is a bluish powder obtained by heating finely divided iridium in air or oxygen. It dissociates above 800°.

Iridous hydroxid, $Ir(HO)_3$, falls as a yellow precipitate when iridium trichlorid is treated with potassium hydroxid.

Iridic oxid, IrO_2, is a black powder obtained by heating iridic hydroxid in carbon dioxid.

Iridic hydroxid, $Ir(HO)_4$, is a blue powder obtained by oxidizing iridous hydroxid or by precipitating the tetrachlorid with potassium hydroxid.

Iridium Halids.—The iridium halids are usually prepared by decomposing the haloiridium salts. The following have been prepared:

$$IrCl_2, \ IrCl_3, \ IrCl_4, \ IrBr_3, \ IrBr_4, \ IrI_3, \ IrI_4.$$

Haloiridium Salts.—Iridium with its valences III and IV forms two series of halo salts, which may be called *haloiridites* and *haloiridates*. Examples are: Potassium chloriridite, $K_3IrCl_6,3H_2O$; ammonium bromiridate, $(NH_4)_2IrBr_6$.

Analagous to these is nitroiridous acid, $H_3Ir(NO_2)_6,H_2O$, and its salts.

Ammonio Iridium Compounds.—These are similar to the ammonio platinum compounds. Examples are: $Ir(NH_3)_2Cl_2$; $Ir(NH_3)_2Cl_4$; and $Ir(NH_3)_6Cl_3$.

Iridium and Sulfur.—Iridium forms three sulfids. The metal burns in sulfur vapor to *iridium monosulfid*, IrS. *Iridous sulfid*, Ir_2S_3, is precipitated from iridous solutions by hydrogen sulfid. *Iridic sulfid*, IrS_2, is a black powder obtained by heating iridium with sulfur and sodium carbonate.

PLATINUM.

Symbol Pt. Atomic weight 195. Valence II and IV. Specific gravity 21.48. Melting-point 1775°.

Occurrence.—Platinum occurs only free in nature, but always alloyed with other metals, chiefly palladium, ruthenium, rhodium, iridium, osmium, gold, silver, iron, and copper. It is mostly found in steel-gray metallic grains, but sometimes in nuggets of several pounds weight. One in the royal cabinet at St. Petersburg weighs fifteen pounds. Platinum comes from the Ural Mountains, and from Brazil, California, Borneo, and Australia.

History.—Platinum seems to have been mentioned in 1558 by Scaliger, who describes it as infusible. It was brought to Europe from South America by Ulloa in 1735. It was described by Watson in 1750, and was afterwards studied by many investigators. The Spaniards called it *platina del Pinto*, platina being the diminutive of plata, which means silver, and the Pinto River in South America being the place from which it was obtained.

Preparation.—Platinum ores are treated with aqua regia, which dissolves platinum, palladium, and rhodium, and leaves the other platinum metals. The platinum is precipitated with ammonium chlorid as ammonium chloroplatinate, which on ignition leaves the metal as spongy platinum. This is compressed and fused in the oxyhydrogen flame.

Physical Properties.—Platinum is a lustrous bluish-white metal of specific gravity 21.48. It is moderately hard and tough, malleable, and very ductile. It is a poor conductor of heat and electricity. It fuses in the oxyhydrogen flame (at 1775°) and partially volatilizes in the electric arc. On cooling from fusion it spits like silver. It softens before fusion and may be welded. At red heat it absorbs hydrogen and allows it to pass through. Spongy platinum and platinum black, which is simply the metal in a fine state of division, absorb large quantities of gases, particularly oxygen (even as much as 250 volumes), and thereby become powerful catalytic agents. A jet of hydrogen impinging against a piece of platinum sponge is inflamed, the condensation of the hydrogen in the presence of the condensed oxygen producing heat enough to cause the union. So a spiral of platinum wire held over an alcohol lamp (best wood alcohol) until red-hot continues to glow after the lamp

is extinguished, being kept hot by the slow oxidation of the alcohol (CH_3OH) to aldehyde (CH_2O). Its specific heat is 0.0314.

Chemical Properties.—Platinum is unchanged in the air hot or cold and dissolves in no acid except aqua regia. It is attacked by hot alkalis and potassium nitrate, and by chlorin, sulfur, phosphorus, silicon, arsenic, and carbon. It may be heated indefinitely in the oxidizing flame, but the colored and smoky flames injure it rapidly.

Platinum Alloys.—Platinum unites with most metals to form alloys which fuse rather easily. Hence neither metals nor metallic compounds which are easily reduced should be heated in platinum vessels. The platinum vessels used in the concentration of sulfuric acid are made more durable by being gilded inside. This is effected by letting molten gold flow over the surface of the red-hot platinum.

Uses.—Platinum is a highly useful metal in laboratories and in the arts and manufactures. It is made into dishes, crucibles, wire, and foil. Its coefficient of expansion is about the same as that of glass, and hence it is well adapted for conveying the electric current through glass. Because of its unalterability it is used for plating other metals, as in chemical balances and various physical apparatus.

Platinum is almost as costly as gold, vessels made of the metal being worth about 60 cents a gram or $17 an ounce.

PLATINUM COMPOUNDS.

The affinity of platinum for oxygen is very weak, and so it has the credit of being chemically inactive. Its compounds, however, are quite numerous, though it does not unite with many of the elements. It acts with valences II and IV to form platinous and platinic compounds. It is basic, but shows acidic tendency in its higher hydroxid and in the halo salts. Thermal equations are $(Pt,H_2,O_2) = 86,300$ cal., $(H_2,Pt,Cl_6,Aq.) = 163,200$ cal., $(H_2,Pt,Cl_4,Aq.) = 120,200$ cal., $(H_2,Pt,Br_6,Aq.) = 113,800$ cal.

Platinum Halids.—Platinum forms halids as follows:

Platinous, ... $PtCl_2$ $PtBr_2$ PtI_2 $Pt(CN)_4$
Platinic, PtF_4 $PtCl_4$ $PtBr_4$ PtI_4

Platinum Chlorid, $PtCl_2$, is a greenish powder obtained by heating chloroplatinic acid to 300°, or by passing dry chlorin over heated platinum sponge. It forms a number of mixed compounds, especially with phosphorous chlorid, phosphorous acid, and carbon monoxid. Of the first two $PtCl_2,PCl_3$ and $PtCl_2,P(HO)_3$ are examples.

Carbonyl Platinum Chlorids.—With carbon monoxid three definite compounds are formed:

Carbonyl platinous chlorid, $PtCl_2CO$, golden-yellow needles.
Dicarbonyl platinum chlorid, $PtCl_2(CO)_2$, pale-yellow needles.
Tricarbonyl platinum chlorid, $PtCl_2(CO)_3$, orange-yellow needles.

Platinic Chlorid, $PtCl_4$, is obtained by dissolving platinum in aqua regia, and separates in red crystals of $PtCl_4,5H_2O$. It is used for potassium determinations in quantitative analysis.

Platinous Bromid, $PtBr_2$, is a brown solid obtained by heating bromplatinic acid.

Platinic Bromid, $PtBr_4$, is a dark-brown powder formed by the action of bromin and hydrobromic acid upon platinum sponge.

Platinous Iodid, PtI_2, is a black powder obtained by heating platinous chlorid with potassium iodid.

Platinic Iodid, PtI_4, is a brown amorphous powder obtained by heating platinic oxid with hydrogen iodid.

Platinous Cyanid, $Pt(CN)_2$, is a greenish-yellow solid obtained by decomposing potassium cyanoplatinite, $K_2Pt(CN)_4$.

Halo Acids and Halo Salts of Platinum.—Platinum is weakly acidic with oxygen, but with the halogens, cyanogen, ammonia, NH_3, and some other radicals it forms numerous salts, and in many cases the corresponding acids.

Haloplatinites.—*Chloroplatinous acid*, H_2PtCl_4 or $\begin{matrix} H{-}Cl = Cl \\ H{-}Cl = Cl \end{matrix}\Big\rangle Pt,$

is formed when platinous chlorid is dissolved in hydrochloric acid. The chloroplatinites are salts of this acid. An example is potassium chloroplatinite, K_2PtCl_4, rose-red crystals used for giving the platinum finish to photographs.

In the same way we have *bromplatinites*, as K_2PtBr_4; *cyanplatinites*, as $K_2Pt(CN)_4$: *nitroplatinites*, as $K_2Pt(NO_2)_4$.

Haloplatinates.—*Chloroplatinic acid*, $\begin{matrix} H{-}Cl = Cl \\ H{-}Cl = Cl \end{matrix}\Big\rangle Pt\Big\langle \begin{matrix} Cl \\ \| \\ Cl \end{matrix}$ or

H_2PtCl_6, is obtained by dissolving platinum in aqua regia. On evaporation it separates in brownish-red crystals of $H_2PtCl_6,6H_2O$. It forms salts with the alkali metals.

Potassium Chloroplatinate, K_2PtCl_6.—This is precipitated as a heavy yellow crystalline powder upon the addition of a potas-

sium salt to chloroplatinic acid. It is slightly soluble in water, from which it crystallizes in octahedrons. It is decomposed by heat into chlorin, potassium chlorid, and platinum, and when strongly heated only platinum remains. It is insoluble in alcohol and serves in analytic chemistry for the separation of potassium from the other alkali metals.

Other salts are *ammonium chloroplatinate*, $(NH_4)_2PtCl_6$; *sodium chloroplatinate*, Na_2PtCl_6; *rubidium chloroplatinate*, Rb_2PtCl_6; *cæsium chloroplatinate*, Cs_2PtCl_6, and *silver chloroplatinate*, Ag_2PtCl_6.

Platinum Oxids and Hydroxids.—Platinum forms two oxids and two hydroxids, all of which have to be prepared indirectly.

Platinous Oxid, PtO, is a gray powder obtained by igniting platinous hydroxid and is decomposed by further heating.

Platinous Hydroxid, $Pt(HO)_2$, is obtained as a black powder by heating platinous chlorid or potassium chloroplatinite with alkali hydroxids.

Platinic Oxid, PtO_2, is a black powder obtained by igniting platinic hydroxid.

Platinic Hydroxid, $Pt(HO)_4$, is obtained as a yellow powder by treating platinic chlorid with hot potassium hydroxid and removing the excess of alkali with acetic acid. It is both basic and acidic, making platinic salts and platinates.

Platinum Sulfids.—*Platinous sulfid*, PtS, is a green powder obtained by direct union of the elements. *Platinic sulfid*, PtS_2, is a gray powder obtained by heating ammonium chloroplatinate with sulfur.

Platinous selenid is also formed by direct union.

Platinum with the Nitroids.—Platinum does not unite with nitrogen, but it forms alloys with phosphorus, arsenic, antimony, bismuth, and vanadium. With phosphorus and arsenic the proportion is approximately PtP_2 and $PtAs_2$.

Platin-ammonia Compounds.—Platinum forms with ammonia a large number of basic compounds, which may be halids, hydroxids, oxids, or salts. The first one of these substances discovered was *platosammonium chlorid*, $Pt(NH_3)_2Cl_2$, known as the *green salt of Magnus*. Isomeric with it is the yellow salt known as the *chlorid of Reiset's second base*. While the structure of these compounds is not certainly known, the suggestions below are probably not very far from the truth :

First type:

	Platinous.	Platinic.
Halid,	$\dfrac{Cl-NH_3}{Cl-NH_4}>Pt.$	$\dfrac{Cl-NH_3}{Cl-NH_3}>Pt<\dfrac{Cl}{Cl}$
Hydroxid,	$\dfrac{H-O-NH_3}{H-O-NH_3}>Pt$	$\dfrac{H-O-NH_3}{H-O-NH_3}>Pt<\dfrac{O-H}{O-H}$
Oxid,	$O<\dfrac{NH_3}{NH_3}>Pt.$	$O<\dfrac{NH_3}{NH_3}>Pt=O$
Salt,	$\dfrac{NO_3-NH_3}{NO_3-NH_3}>Pt.$	$SO_4<\dfrac{NH_3}{NH_3}>Pt=SO_4$

Second type (isomeric with·the above):
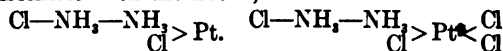
$$\underset{Cl}{Cl-NH_3-NH_3}>Pt. \qquad \underset{Cl}{Cl-NH_3-NH_3}>Pt<\dfrac{Cl}{Cl}$$

Third type:

$$\dfrac{Cl-NH_3-NH_3}{Cl-NH_3}>Pt. \qquad \dfrac{Cl-NH_3-NH_3}{Cl-NH_3}>Pt<\dfrac{Cl}{Cl}$$

Fourth type:

$$\dfrac{Cl-NH_3-NH_3}{Cl-NH_3-NH_3}>Pt. \qquad \dfrac{Cl-NH_3-NH_3}{Cl-NH_3-NH_3}>Pt<\dfrac{Cl}{Cl}$$

Fifth type:

$$Cl-NH-_3Pt. \qquad Cl-NH_3-PtCl_2$$
$$Cl-NH_3-\overset{|}{P}t \qquad Cl-NH_3-\overset{|}{P}tCl_4$$

Sixth type:

$$(Cl-NH_3)_2=Pt-Cl$$
$$(Cl-NH_3)_2=\overset{|}{P}t-Cl$$

Seventh type:

$$Cl-NH_3-NH_3-Pt \qquad Cl-NH_3-NH_3-PtCl_2$$
$$Cl- \qquad NH_3-\overset{|}{P}t \qquad Cl-NH_3-\overset{|}{P}tCl_2$$

Eighth type:

$$Cl-NH_3-NH_3-Pt \qquad Cl-NH_3-NH_3-PtCl_2$$
$$Cl-NH_3-NH_3-\overset{|}{P}t \qquad Cl-NH_3-NH_3-\overset{|}{P}tCl_2$$

Ninth type:

$$(Cl-NH_3-NH_3)_2=PtCl$$
$$(Cl-NH_3-NH_3)_2=\overset{|}{P}tCl$$
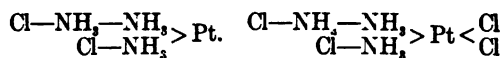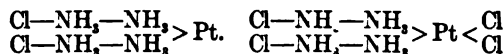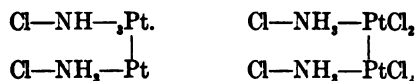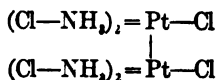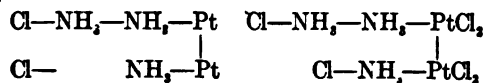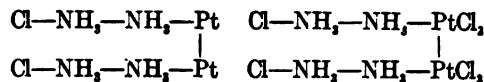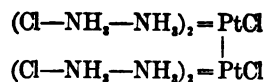
There are also compounds containing more than two platinum atoms.

CHAPTER XL.

RADIUM, POLONIUM, AND ACTINIUM.

THE radioactivity of the ores and compounds of uranium, thorium, rhodium, barium, etc., is thought to be due to the presence in small quantities of radioactive elements. In 1898 Monsieur Pierre and Madame Sklodowska Curie of Paris announced the discovery in pitchblende of a new element which they called *polonium*, after Poland, the native country of Mme. Curie. In 1899 the Curies, in connection with Monsieur G. Bemont, found another element which they called *radium*, because of its radioactivity. In 1899 André Debierne found in the residues from pitch blend, in addition to radium and polonium, a third radioactive substance for which he suggested the name *actinium*. This substance is also found associated with thorium, and the radioactivity of thorium compounds is thought to be due to it. Radium is related in properties to barium, polonium to bismuth, and actinium to thorium.

Radioactive substances have been carefully investigated by many chemists and physicists. Especially notable is the work of M. and Mme. Curie upon radium. None of these elements have been isolated, but definite compounds of radium have been prepared.

The Curies obtained radium compounds from the residues of the uranium factory of Joachimsthal, Bohemia. The separation is effected by a long and complicated process of precipitation and fractional crystallization, and only a few grains are obtained from a ton of the ore. The compounds closely resemble those of barium. The atomic weight assigned to radium is 225, though Runge obtained from its spectrum the number 256. It has a characteristic spectrum and an intense radioactivity. Its place in the periodic table is in Group II below barium and in the series with thorium and uranium.

Radium emits emanations and rays such as have been described in Photochemistry. It preserves a temperature one or more degrees above that of the atmosphere, injures the eyes, and disorganizes the flesh when kept long in contact with it. Its peculiar properties have been explained in various ways. The most plausible suggestion is that atoms of high atomic weight slowly disintegrate into ultimate corpuscles or particles and that this decomposition is attended with the development of great energy.

APPENDIX.

WEIGHTS AND MEASURES.

THE following abbreviations are used:

mm., millimeter.	qmm., square millimeter.	cmm., cubic millimeter.
cm., centimeter.	qcm., square centimeter.	cc., cubic centimeter.
m., meter.	qm., square meter.	cbm., cubic meter.
l., liter.	g., gram.	k., kilogram.
mg., milligram.	cg., centigram.	dg., decigram.

Equivalents:

1 meter	=	3.2809 feet.	1 foot	=	0.30479 meter.
1 meter	=	39.37079 inches.	1 inch	=	25.3995 mm.
1 cm.	=	0.3937 inch.	1 foot	=	30.479 cm.
1 mm.	=	0.03937 inch.	1 yard	=	0.91438 meter.
1 kilometer	=	0.6214 mile.	1 mile	=	1609.31 meters.
1 qmm.	=	0.00155 sq. ins.	1 sq. inch	=	6.4514 qcm.
1 qcm.	=	0.15501 sq. ins.	1 sq. foot	=	929. qcm.
1 liter	=	61.027 cu. ins.	1 cu. inch	=	16.386 cc.
1 liter	=	0.26419 U.S. gal.	1 gallon	=	3.7852 liters.
1 liter	=	1.05676 quart.	1 quart	=	0.9463 liter.
1 liter	=	2.11352 pint	1 pint	=	473.15 cc.
1 cc.	=	0.0338 fluid oz.	1 fluid oz	=	29.572 cc.
1 cbm.	=	264.19 U.S. gals.	1000 gals.	=	3.7852 cm.
1 gram	=	15.4346 grains.	1 grain	=	0.0648 gram.
1 mg.	=	0.01543 grain.	1 grain	=	62.799 mg.
100 grams	=	3.5274 ozs. av.	1 oz. av.	=	28.3495 grams.
1 kilogram	=	2.2046 pounds.	1 pound	=	453.59 grams.
1000 kg.	=	1.1023 tons.	1 ton	=	907.2 kg.

Conversion of thermometer degrees:

C. = Centigrade. F. = Fahrenheit. R. = Réaumur.

F. to C., subtract 32°, then multiply by 5 and divide by 9.

F. to R., subtract 32°, then multiply by 4 and divide by 9.

R. to C., multiply by 5 and divide by 4.

R. to F., multiply by 9 and divide by 4, then add 32°.

C. to F., multiply by 9 and divide by 5, then add 32°.

C. to R., multiply by 4 and divide by 5.

SOLUTIONS.

A normal solution is one which contains in a liter a number of grams of any substance equal to its chemical equivalent in terms of the hydrogen atom. The chemical equivalent of sulfuric acid is 49, or one half the molecular weight, because the acid is dibasic. One liter of normal sulfuric acid contains 49 grams of H_2SO_4. The normal strength is indicated by the letter N, while 5N and $\frac{N}{10}$ mean five times normal and one tenth normal respectively.

All solutions kept in the laboratory should be of known strength, and it is generally most convenient to make them some multiple or fraction of the normal. The more common solutions are here given in the suitable strength.

Sulfuric Acid, H_2SO_4: equivalent 49, specific gravity 1.84, 36N.

Dilute: Sp. gr. 1.18, 5N, 24.5 per cent H_2SO_4, 1 vol. strong acid to 6 of water. This is the strength suitable for making hydrogen, while an acid of half this strength is best for hydrogen sulfid.

Nitric Acid, HNO_3: equivalent 63, sp. g. 1.42, 16N, 65 per cent HNO_3.

Dilute: Sp. gr. 1.2, 5N, 30 per cent HNO_3, 1 vol. strong acid to 2 of water.

Hydrochloric Acid, HCl: equivalent 36.4, sp. gr. 1.16, 10N, 32.2 per cent HCl.

Dilute: Sp. gr. 1.09, 5N, 18.4 per cent HCl, 1 vol. strong acid to 1 of water.

Acetic Acid, $C_2H_4O_2$: equivalent 60, glacial 17N.

Dilute: Sp. gr. 1.04, 5N, 30 per cent $C_2H_4O_2$, 1 vol. glacial acid to $2\frac{1}{2}$ vols. water.

Ammonia Solution, NH_4HO: equivalent 35, sp. gr. 0.9, 20N, 60 per cent NH_4OH.

Dilute: Sp. gr. 0.965, 5N, 17.5 per cent NH_4HO, 1 vol. strong ammonia to 3 of water.

Potassium Hydroxid, KHO: equivalent 56; 280 grams dissolved in 1 liter water = 5N, sp. gr. 1.265, 28 per cent KHO.

Sodium Hydroxid, NaHO: equivalent 40; 200 grams dissolved in water and made 1 liter = 5N, sp. gr. 1.24, 20 per cent NaHO.

Ammonium Sulfid, $(NH_4)_2S$: equivalent 34. Saturate 600 cc. 5N ammonia with H_2S and add 400 cc 5N ammonia. This solution does not keep, but gradually decomposes with formation of yellow ammonium sulfid, $(NH_4)_2S_2$.

Ammonium Chlorid, NH_4Cl: equivalent 53.4; 267 grams dissolved in 1 liter of water = 5N, 26.7 per cent NH_4Cl.

Ammonium Carbonate, $(NH_4)_2CO_3$: equivalent 48. Dissolve 200

grams of commercial ammonium carbonate in 350 cc. 5N ammonia and dilute with water to 1 liter = 5N.

Solutions of salts are generally made normal if they are sufficiently soluble. The following are less than normal:

Ammonium Oxalate, $(NH_4)_2C_2O_4,2H_2O$: equivalent 80, solution $\dfrac{N}{2}$.

Barium Hydroxid, $BaH_2O_2,8H_2O$: equivalent 157.5, solution $\dfrac{N}{5}$.

Calcium Hydroxid, CaH_2O_2: equivalent 37, saturated solution $\dfrac{N}{20}$.

Mercuric Chlorid, $HgCl_2$: equivalent 135.4, solution $\dfrac{N}{5}$.

Mercurous Nitrate, $Hg_2(NO_3)_2,2H_2O$: equivalent 280; 56 grams dissolved in 40 cc. 5N HNO_3 and diluted to 1 liter makes $\dfrac{N}{5}$ solution. A few drops of mercury is added to the bottle.

Potassium Iodid, KI: equivalent 166, solution $\dfrac{N}{5}$.

Potassium Bromid, KBr: equivalent 119, solution $\dfrac{N}{5}$.

Silver Nitrate, $AgNO$: equivalent 170, solution $\dfrac{N}{5}$.

Bromin Water: equivalent 80, saturated solution $\dfrac{N}{2}$.

Chlorin Water: equivalent 35.4, saturated solution $\dfrac{N}{5}$.

SPECIAL SOLUTIONS.

Magnesia Mixture.—Dissolve 66 grams magnesium chlorid and 168 grams ammonium chlorid in 400 cc. water, add 300 cc. 5N ammonia and make up to 1 liter.

Molybdate Solution.—Dissolve 100 grams molybdic oxid in 400 cc. 5N ammonia and pour, with stirring, into 1000 cc. 5N HNO_3.

Fehling's Solution.—Dissolve 34.64 grams copper sulfate in 500 cc. water; also dissolve 180 grams sodium potassium tartrate, Rochelle salt, and 70 grams caustic soda in 500 cc. water. Mix the solutions in equal parts as needed.

Nessler's Reagent.—Dissolve 35 grams potassium iodid and 13 grams mercuric chlorid in 800 cc. water. Add saturated solution of mercuric chlorid until the red precipitate is just persistent. Add 160 grams caustic potash and dilute to 1000 cc. To keep the solution sensitive add from time to time a little more mercuric chlorid.

1908.

TABLE OF INTERNATIONAL ATOMIC WEIGHTS.

Name.	Sym.	O=16.	H=1.	Name.	Sym.	O=16.	H=1.
Aluminium	Al	27.1	26.9	Molybdenum ...	Mo	96.0	95.3
Antimony	Sb	120.2	119.3	Neodymium	Nd	143.6	142.5
Argon	A	39.9	39.6	Neon	Ne	20.	19.9
Arsenic	As	75.0	74.4	Nickel	Ni	58.7	58.3
Barium	Ba	137.4	136.4	Nitrogen	N	14.01	13.91
Bismuth	Bi	208.0	206.3	Osmium	Os	191.	189.6
Boron	B	11.	10.9	Oxygen	O	16.00	15.88
Bromine	Br	79.96	79.36	Palladium	Pd	106.5	105.7
Cadmium	Cd	112.4	111.6	Phosphorus	P	31.0	30.77
Cæsium	Cs	132.9	131.9	Platinum	Pt	194.8	193.3
Calcium.......	Ca	40.1	39.7	Potassium......	K	39.15	38.85
Carbon	C	12.00	11.91	Praseodymium..	Pr	140.5	139.4
Cerium	Ce	140.25	139.2	Radium........	Ra	225.	223.3
Chlorine	Cl	35.45	35.18	Rhodium	Rh	103.0	102.2
Chromium	Cr	52.1	51.7	Rubidium	Rb	85.5	84.9
Cobalt	Co	59.0	58.55	Ruthenium	Ru	101.7	100.9
Columbium....	Cb	94.	93.3	Samarium	Sa	150.3	149.2
Copper	Cu	63.6	63.1	Scandium	Sc	44.1	43.8
Dysprosium ...	Dy	162.5	161.2	Selenium	Se	79.2	78.6
Erbium	E	166.	164.8	Silicon	Si	28.4	28.2
Europium	Eu	152.	150.8	Silver..........	Ag	107.93	107.11
Fluorine	F	19.	18.9	Sodium	Na	23.05	22.88
Gadolinium ...	Gd	156.	154.8	Strontium	Sr	87.6	86.94
Gallium	Ga	70.	69.5	Sulphur	S	32.06	31.82
Germanium ...	Ge	72.5	72.	Tantalum	Ta	181.	179.6
Glucinum	Gl	9.1	9.03	Tellurium	Te	127.6	126.6
Gold	Au	197.2	195.7	Terbium	Tb	159.	157.7
Helium	He	4.	4.	Thallium	Tl	204.1	202.6
Hydrogen	H	1.008	1.000	Thorium	Th	232.5	230.8
Indium	In	115.	114.1	Thulium	Tm	171.	169.7
Iodine	I	126.97	126.01	Tin.............	Sn	119.0	118.1
Iridium	Ir	193.0	191.5	Titanium	Ti	48.1	47.7
Iron	Fe	55.9	55.5	Tungsten	W	184.0	182.6
Krypton	Kr	81.8	81.2	Uranium	U	238.5	236.7
Lanthanum ...	La	138.9	137.9	Vanadium......	V	51.2	50.8
Lead	Pb	206.9	205.35	Xenon	Xe	128.	127.
Lithium	Li	7.03	6.98	Ytterbium	Yb	173.0	171.7
Magnesium	Mg	24.36	24.18	Yttrium	Y	89.0	88.3
Manganese	Mn	55.0	54.6	Zinc	Zn	65.4	64.9
Mercury	Hg	200.0	198.5	Zirconium	Zr	90.6	89.9

BIOGRAPHICAL INDEX.

INDEX.

SHORT-TITLE · CATALOGUE

OF THE

PUBLICATIONS

OF

JOHN WILEY & SONS,

NEW YORK.

LONDON: CHAPMAN & HALL, LIMITED.

ARRANGED UNDER SUBJECTS.

Descriptive circulars sent on application. Books marked with an asterisk (*) are sold at *net* prices only. All books are bound in cloth unless otherwise stated.

AGRICULTURE—HORTICULTURE—FORESTRY.

Armsby's Principles of Animal Nutrition 8vo, $4 00
Budd and Hansen's American Horticultural Manual:
    Part I. Propagation, Culture, and Improvement................12mo, 1 50
    Part II. Systematic Pomology...............................12mo, 1 50
Elliott's Engineering for Land Drainage.........................12mo, 1 50
    Practical Farm Drainage 2d Edition. Rewritten...............12mo, 1 50
Graves's Forest Mensuration. 8vo, 4 00
Green's Principles of American Forestry.........................12mo, 1 50
Grotenfelt's Principles of Modern Dairy Practice. (Woll)....... 12mo, 2 00
* Herrick's Denatured or Industrial Alcohol.....................8vo, 4 00
Kemp and Waugh's Landscape Gardening. New Edition, Rewritten. (In
      Preparation.)
* McKay and Larsen's Principles and Practice of Butter-making 8vo, 1 50
Maynard's Landscape Gardening as Applied to Home Decoration. 12mo, 1 50
Quaintance and Scott's Insects and Diseases of Fruits. (In Preparation).
Sanderson's Insects Injurious to Staple Crops. 12mo, 1 50
* Schwarz's Longleaf Pine in Virgin Forests.......................12mo, 1 25
Stockbridge's Rocks and Soils.....................................8vo, 2 50
Winton's Microscopy of Vegetable Foods. 8vo, 7 50
Woll's Handbook for Farmers and Dairymen. 16mo, 1 50

ARCHITECTURE.

Baldwin's Steam Heating for Buildings. 12mo, 2 50
Berg's Buildings and Structures of American Railroads...............4to, 5 00
Birkmire's Architectural Iron and Steel...........................8vo, 3 50
    Compound Riveted Girders as Applied in Buildings...............8vo, 2 00
    Planning and Construction of American Theatres.................8vo, 3 00
    Planning and Construction of High Office Buildings. 8vo, 3 50
    Skeleton Construction in Buildings. 8vo, 3 00
Briggs's Modern American School Buildings.........................8vo, 4 00
Byrne's Inspection of Material and Wormanship Employed in Construction.
                                             16mo, 3 00
Carpenter's Heating and Ventilating of Buildings. 8vo, 4 00
* Corthell's Allowable Pressure on Deep Foundations 12mo, 1 25

1

ARMY AND NAVY.

2.

ASSAYING.

ASTRONOMY.

CHEMISTRY.

5

CIVIL ENGINEERING.

BRIDGES AND ROOFS. HYDRAULICS. MATERIALS OF ENGINEER-
ING. RAILWAY ENGINEERING.

BRIDGES AND ROOFS.

HYDRAULICS.

8

MATERIALS OF ENGINEERING.

Wood's (De V.) Treatise on the Resistance of Materials, and an Appendix on
the Preservation of Timber. 8vo, 2 00
Wood's (M. P.) Rustless Coatings: Corrosion and Electrolysis of Iron and
Steel. 8vo, 4 00

RAILWAY ENGINEERING.

Andrews's Handbook for Street Railway Engineers ....3x5 inches, mor. 1 25
Berg's Buildings and Structures of American Railroads 4to, 5 00
Brooks's Handbook of Street Railroad Location. ....16mo, mor. 1 50
Butt's Civil Engineer's Field-book. ....16mo, mor. 2 50
Crandall's Railway and Other Earthwork Tables. 8vo, 1 50
Transition Curve. ....16mo, mor. 1 50
* Crockett's Methods for Earthwork Computations....................8vo, 1 50
Dawson's "Engineering" and Electric Traction Pocket-book......16mo, mor. 5 00
Dredge's History of the Pennsylvania Railroad: (1879).............Paper, 5 00
Fisher's Table of Cubic Yards...............................Cardboard, 25
Godwin's Railroad Engineers' Field-book and Explorers' Guide... 16mo, mor. 2 50
Hudson's Tables for Calculating the Cubic Contents of Excavations and Em-
bankments. 8vo, 1 00
Ives and Hilts's Problems in Surveying, Railroad Surveying and Geodesy
16mo, mor. 1 50
Molitor and Beard's Manual for Resident Engineers. 16mo, 1 00
Nagle's Field Manual for Railroad Engineers. ....16mo, mor. 3 00
Philbrick's Field Manual for Engineers. ....16mo, mor. 3 00
Raymond's Railroad Engineering. 3 volumes.
Vol. I. Railroad Field Geometry. (In Preparation.)
Vol. II. Elements of Railroad Engineering....................8vo, 3 50
Vol. III. Railroad Engineer's Field Book. (In Preparation.)
Searles's Field Engineering. ....16mo, mor. 3 00
Railroad Spiral ....16mo, mor. 1 50
Taylor's Prismoidal Formulæ and Earthwork........................8vo, 1 50
* Trautwine's Field Practice of Laying Out Circular Curves for Railroads.
12mo. mor. 2 50
* Method of Calculating the Cubic Contents of Excavations and Embank-
ments by the Aid of Diagrams. 8vo, 2 00
Webb's Economics of Railroad Construction..................Large 12mo, 2 50
Railroad Construction...................................16mo, mor. 5 00
Wellington's Economic Theory of the Location of Railways. ......Small 8vo, 5 00

DRAWING.

Barr's Kinematics of Machinery....................................8vo, 2 50
* Bartlett's Mechanical Drawing....................................8vo, 3 00
*   "   "   "   Abridged Ed. 8vo, 1 50
Coolidge's Manual of Drawing. ....8vo, paper, 1 00
Coolidge and Freeman's Elements of General Drafting for Mechanical Engi-
neers...Oblong 4to, 2 50
Durley's Kinematics of Machines....................................8vo, 4 00
Emch's Introduction to Projective Geometry and its Applications........8vo, 2 50
Hill's Text-book on Shades and Shadows, and Perspective. 8vo, 2 00
Jamison's Advanced Mechanical Drawing...........................8vo, 2 00
Elements of Mechanical Drawing..............................8vo, 2 50
Jones's Machine Design:
Part I. Kinematics of Machinery..............................8vo, 1 50
Part II. Form, Strength, and Proportions of Parts. 8vo, 3 00
MacCord's Elements of Descriptive Geometry.......................8vo, 3 00
Kinematics; or, Practical Mechanism. 8vo, 5 00
Mechanical Drawing. 4to, 4 00
Velocity Diagrams. 8vo, 1 50

10

ELECTRICITY AND PHYSICS.

MECHANICAL ENGINEERING.

MATERIALS OF ENGINEERING, STEAM-ENGINES AND BOILERS.

13

14

Maire's Modern Pigments and their Vehicles.........................12mo, 2 00
Martens's Handbook on Testing Materials. (Henning)................8vo, 7 50
Maurer's Technical Mechanics. 8vo, 4 00
Merriman's Mechanics of Materials................................8vo, 5 00
*   Strength of Materials 12mo, 1 00
Metcalf's Steel. A Manual for Steel-users........................12mo, 2 00
Sabin's Industrial and Artistic Technology of Paints and Varnish.......8vo, 3 00
Smith's Materials of Machines....................................12mo, 1 00
Thurston's Materials of Engineering... ....3 vols., 8vo, 8 00
      Part I.   Non-metallic Materials of Engineering and Metallurgy...8vo, 2 00
      Part II. , Iron and Steel.......................................8vo, 3 50
      Part III. A Treatise on Brasses, Bronzes, and Other Alloys and their
            Constituents.....,.......................................8vo, 2 50
Wood's (De V.) Elements of Analytical Mechanics. 8vo, 3 00
      Treatise on the Resistance of Materials and an Appendix on the
            Preservation of Timber 8vo, 2 00
Wood's (M. P.) Rustless Coatings: Corrosion and Electrolysis of Iron and
            Steel...8vo, 4 00

STEAM-ENGINES AND BOILERS.

Berry's Temperature-entropy Diagram.............................12mo, 1 25
Carnot's Reflections on the Motive Power of Heat. (Thurston).......12mo, 1 50
Chase's Art of Pattern Making...................................12mo, 2 50
Creighton's Steam-engine and other Heat-motors............... ... .8vo, 5 00
Dawson's "Engineering" and Electric Traction Pocket-book.....16mo, mor. 5 00
Ford's Boiler Making for Boiler Makers............................18mo, 1 00
Gebhardt's Steam Power Plant Engineering. (In Press.)
Goss's Locomotive Performance.... ....8vo, 5 00
Hemenway's Indicator Practice and Steam-engine Economy..........12mo, 5 00
Hutton's Heat and Heat-engines...................................8vo, 5 00
      Mechanical Engineering of Power Plants. 8vo, 5 00
Kent's Steam boiler Economy......................................8vo, 4 00
Kneass's Practice and Theory of the Injector........................8vo, 1 50
MacCord's Slide-valves...8vo, 2 00
Meyer's Modern Locomotive Construction. 4to, 10 00
Moyer's Steam Turbines. (In Press.)
Peabody's Manual of the Steam-engine Indicator....................12mo, 1 50
      Tables of the Properties of Saturated Steam and Other Vapors. 8vo, 1 00
      Thermodynamics of the Steam-engine and Other Heat-engines......8vo, 5 00
      Valve-gears for Steam-engines. 8vo, 2 50
Peabody and Miller's Steam-boilers. 8vo, 4 00
Pray's Twenty Years with the Indicator.......................Large 8vo, 2 50
Pupin's Thermodynamics of Reversible Cycles in Gases and Saturated Vapors.
      (Osterberg)..12mo, 1 25
Reagan's Locomotives: Simple, Compound, and Electric. New Edition.
                                                Large 12mo, 3 50
Sinclair's Locomotive Engine Running and Management.............12mo, 2 00
Smart's Handbook of Engineering Laboratory Practice..............12mo, 2 50
Snow's Steam-boiler Practice.....................................8vo, 3 00
Spangler's Notes on Thermodynamics...............................12mo, 1 00
      Valve-gears..8vo, 2 50
Spangler, Greene, and Marshall's Elements o Steam-engineering.......8vo, 3 00
Thomas's Steam-turbines...8vo, 4 00
Thurston's Handbook of Engine and Boiler Trials, and the Use of the Indi-
            cator and the Prony Brake. 8vo, 5 00
      Handy Tables. 8vo, 1 50
      Manual of Steam-boilers, their Designs, Construction, and Operation..8vo, 5 00
15

MECHANICS PURE AND APPLIED.

MEDICAL.

METALLURGY.

MINERALOGY.

MINING.

SANITARY SCIENCE.

MISCELLANEOUS.

HEBREW AND CHALDEE TEXT-BOOKS.

19